

APPENDIX B

DOCUMENTATION OF  
A GAS PHASE PHOTOCHEMICAL MECHANISM  
FOR USE IN AIRSHED MODELING

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## ABSTRACT

This report documents the updated gas-phase mechanisms which were developed as part of an overall contract for the development and implementation of such mechanisms for use in airshed modeling. A series of mechanisms, which are consistent in their common reactions but which vary in level of condensation, are described. These mechanisms used the detailed SAPRC/ERT mechanism as a starting point, but were updated based on the results of the most recent evaluations of relevant laboratory data. The most detailed mechanism was evaluated using the data base of over 500 environmental chamber experiments used to evaluate the SAPRC/ERT mechanism, and its performance in simulating these experiments is comparable to the previous mechanism. The more condensed mechanisms, which vary in level of detail both with regard to the number of lumped species used to represent primary emitted organics, and the number of species used to represent reactive products, were compared with the detailed mechanism in an extensive series of test calculations. These include calculations using as input the full mix of emitted species into California air basins (for the 1983 inventory), as well as calculations simulating the reactions of individual types of emitted compounds and reactive product species. The results of these test calculations permit the airshed model user to chose the level of condensation of the mechanism which is most appropriate to specific airshed model applications.

In order to represent the reactions of the range of organics emitted into the atmosphere, the most detailed mechanism includes separate reactions or estimated mechanistic parameters for over 100 "detailed model species." Assignments of these species were made for over 350 categories of organics used in present ARB emissions inventories. This accounts for essentially all the mass of identified organic emissions into California air basins in the 1983 emissions inventories. These detailed emissions assignments can be used as a basis for deriving kinetic and mechanistic parameters for the lumped species in the condensed mechanisms used in airshed models.



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## I. INTRODUCTION

In recent years the use of computer models has become widespread for prediction of the impacts of chemical emissions on the ecosystem. In particular, computer models incorporating chemistry, transport, and meteorology are becoming routine tools for the assessment of present and proposed future emission control strategies. Since the implementation of most emission control strategies ultimately involve the expenditure of millions, if not billions, of dollars, it is clearly necessary that the emissions inventories, atmospheric chemical mechanisms, and meteorological parameters in these complex computer models are the best available, and that they be continually updated. This is especially true of the chemical mechanism component of the overall computer model, since data from laboratory and environmental chamber studies are continually and rapidly advancing our state of knowledge concerning the atmospheric chemistry of anthropogenic and biogenic emissions.

During consultations with the California Air Resources Board (ARB) modeling staff, it became apparent, both to the ARB modelers and to ourselves, that there was a need to update the chemical mechanisms incorporated in the airshed models that the ARB staff have been using for control strategy assessment. To address this need, the Statewide Air Pollution Research Center (SAPRC) carried out a two-year research program to update the detailed chemical mechanism which was developed at SAPRC, and to condense and adapt it for use in airshed models. The resulting detailed and condensed mechanisms are documented in this report.

The detailed mechanism which was used as the starting point in this program was the mechanism that SAPRC developed under previous EPA and USAF funding. Under funding from the EPA, SAPRC developed a detailed photochemical transformation mechanism and evaluated it against over 500 environmental chamber experiments carried out at the facilities at SAPRC and the University of North Carolina (UNC) [Carter et al. 1986, Lurmann et al. 1987a]. This was adapted and condensed for use in airshed models by ERT (Lurmann et al. 1987a,b), and the resulting mechanism is known as the "SAPRC/ERT" mechanism. Under USAF funding, this mechanism was extended to include reactions of compounds not on the EPA-funded mechanism, and

initial work on the related problem of representing complex mixtures in such mechanisms was also carried out (Carter et al. 1987).

Although this mechanism provided a good starting point, a number of extensions and modifications to it were required in order to address the needs of the ARB modeling staff. These were as follows: (1) the mechanism needed to be updated to take into account the results of the latest evaluations of the available relevant data, including the comprehensive evaluation being carried out by Atkinson as part of this program; (2) the mechanism needed to be extended to include representations of the reactions of biogenic organics, methanol, ethanol, and other types of emitted organics which were not explicitly represented in the existing lumped SAPRC/ERT mechanism, as well as gas-phase  $\text{SO}_2$  reactions; (3) procedures for assigning the many types of emitted species into the lumped species in the mechanism needed to be refined; and (4) the updated and extended mechanism needed to be condensed for use in airshed models. These needs were addressed as a part of this program.

The modifications and extensions of the SAPRC/ERT mechanism which were made to address the requirements of the ARB are documented in this volume. In Section II, the updated detailed mechanism is documented, and its performance in simulating the results of the approximately 500 chamber experiments used in evaluating the previous mechanisms is summarized. This includes documentation of the kinetic and mechanistic parameters for the over 100 "detailed model species" used to represent the complex mixtures of organics present in emissions inventories. In Section III, the assignments of these detailed model species to approximately 350 of the detailed chemical categories used in current emissions inventories is summarized, and some of the difficulties encountered in this process are described. In Section IV, a number of condensed versions of the detailed mechanism, which are suitable for use in airshed models, are documented, and the results of an extensive series of test calculations comparing the condensed mechanisms with the more detailed mechanism are summarized. Finally, a summary of the conclusions resulting from this work is given in Section V.

## II. DOCUMENTATION OF THE UPDATED DETAILED REACTION MECHANISM

The starting point for the detailed mechanism documented in this section was the detailed mechanisms which had previously been documented in reports to the EPA (Carter et al. 1986; Lurmann et al. 1987a) and the USAF (Carter et al. 1987). The primary difference between the mechanism documented for the USAF and the version documented for the EPA is that the EPA version employed a limited number of lumped species with fixed mechanistic parameters, while the USAF version included assignments for a large number of individual alkanes, aromatics, alkenes, and other species, with these compounds then being represented in the mechanism using generalized species and reactions with parameters derived based on the compound(s) being represented. The mechanism documented here follows the approach of the USAF version. Kinetic and mechanistic assignments were made for over 100 compounds representative of those occurring in present emissions profiles, and these assignments then serve as a basis for deriving the parameters used in both the detailed and condensed mechanisms. In the condensed mechanisms, documented in the section IV, a limited number of model species are used to represent compounds, with parameters derived based on the specific mixtures being represented. In the most detailed mechanism, discussed in this section, each of these species, which are referred to as "detailed model species," is considered as being represented separately in the model.

The previous mechanisms documented for the EPA and the USAF were essentially the same in the species employed to represent the reactions of the inorganics species and the reactive organic products and radical intermediates, and this mechanism follows the same general approach in these regards. This mechanism also follows a similar approach in the treatment of the major uncertain areas of the mechanism and in the treatment of chamber effects used when evaluating the mechanism against chamber data. Therefore, a discussion of these approaches, the reasons for using them, and the uncertainties and approximations involved, are not given here, and the reader is referred to previous reports for more details in these regards. In particular, Carter et al. (1986) gives the most detailed discussion of all the various aspects of the mechanism and the uncertainties involved (including areas where parameters had to be

derived based on fits to chamber data, and detailed discussions of the treatments of chamber effects), while the more recent reports of Lurmann et al. (1987a) and Carter et al. (1987) describe the approach used in the current mechanism for representing the reactions of the aromatic hydrocarbons and the reactions of the peroxy radical intermediates.

The major modifications to the detailed mechanism which were made for this program concerned updating individual constants and other parameters, and extending the number of detailed model species for which parameters are assigned. The updates are based primarily on the most recent reviews of relevant kinetic and mechanistic laboratory data given by NASA (1987), CODATA (Baulch et al. 1986), and Atkinson (1986, 1988). The comprehensive review of Atkinson (1988), carried out as part of this program, was particularly useful in this regard. The extensions included adding reactions of compounds such as methanol, ethanol, other alcohols and ethers, biogenically emitted alkenes, and other types of compounds or model species representing those in emissions profiles, but not included in the previous mechanism documented for the USAF (Carter et al. 1987).

A complete listing of the detailed mechanism, documenting the sources of all rate constants and mechanistic assignments used, is given in Section II.A, below. Then, in Section II.B, the performance of the updated detailed mechanism in simulating the results of the over 500 chamber runs used to evaluate the previous mechanisms is summarized.

#### A. Complete Listing of the Detailed Mechanism

The current detailed SAPRC gas phase atmospheric photochemical transformation mechanisms are given in Tables 1 through 9. The species used explicitly in the mechanism are listed in Table 1, and their reactions and rate constant parameters are listed in Table 2. The absorption coefficients and quantum yields used in the photolysis reactions in Table 2 are listed in Table 3. As indicated above, a set of generalized reactions, with variable kinetic and mechanistic parameters, are used to represent reactions of individual alkane, aromatic, alkene (other than ethene), and other species. The types of parameters used for alkane and aromatic species are summarized in Table 4, and the types of parameters used for alkene species are summarized in Table 5. The kinetic and mechanistic parameters assigned for the individual alkane species are

given in Table 6, the parameters assigned for the aromatics are given in Table 7, the parameters assigned for alcohols, ethers, and other miscellaneous species estimated to react with mechanisms similar to alkanes are given in Table 8, and the parameters assigned for the alkenes are given in Table 9. Some of these detailed model species represent individual compounds, while others represent groups of compounds which are estimated to have similar reactivity. The use of these detailed species in representing the organics present in emissions profiles is discussed in Section III.

The tables documenting the mechanism include comments giving the sources of the rate constants and mechanistic assignments used in this mechanism. Table 2 includes comments following each individual reaction in the mechanism, giving the source used for the rate constant, absorption coefficients and quantum yields and (where applicable) the distribution of products assumed in the mechanism. Comments or footnotes in Tables 6 through 9 give the sources used or methods for deriving the kinetic and mechanistic parameters for the individual species listed there. The references cited in these comments should be consulted for further documentation of the rate constants, mechanisms, or absorption coefficients and quantum yields which were employed, and their associated uncertainties.

Table 1. List of Species in the Detailed Mechanism

| No.                            | Name | Description  |
|--------------------------------|------|--|
| ACTIVE INORGANIC SPECIES       |      |  |
| 1                              | O3   | Ozone  |
| 2                              | NO   | Nitric oxide   |
| 3                              | NO2  | Nitrogen dioxide   |
| 4                              | NO3  | NO <sub>3</sub> radicals   |
| 5                              | N2O5 | N <sub>2</sub> O <sub>5</sub>  |
| 6                              | HNO3 | Nitric acid  |
| 7                              | HONO | Nitrous acid   |
| 8                              | HNO4 | Peroxynitric acid  |
| 9                              | HO2. | HO <sub>2</sub> radicals   |
| 12                             | CO   | Carbon monoxide  |
| 10                             | HO2H | Hydrogen peroxide (Can be made "product only" if appropriate)  |
| 11                             | SO2  | Sulphur dioxide (Can be removed if appropriate)  |
| ACTIVE ORGANIC PRODUCT SPECIES |      |  |
| 13                             | HCHO | Formaldehyde   |
| 14                             | CCHO | Acetaldehyde   |
| 15                             | PAN  | Peroxy acetyl nitrate  |
| 16                             | RCHO | Propionaldehyde and lumped higher aldehydes  |
| 17                             | PPN  | Peroxy propionyl nitrate and higher PAN analogues  |
| 18                             | ACET | Acetone  |
| 19                             | MEK  | Methylethyl ketone and lumped higher ketones   |
| 20                             | RNO3 | Lumped organic nitrates  |
| 21                             | GLY  | Glyoxal  |
| 22                             | GPAN | PAN analogue formed from glyoxal   |
| 23                             | MGLY | Methyl glyoxal   |
| 24                             | PHEN | Phenol   |
| 25                             | CRES | Cresols and other alkyl phenols  |
| 26                             | BALD | Benzaldehyde and other aromatic aldehydes  |
| 27                             | PBZN | Peroxy benzoyl nitrate   |
| 28                             | NPHE | Nitrophenols and other aromatic nitro-compounds  |
| 29                             | AFG1 | Unknown aromatic fragmentation product #1. (Formed from benzene, tetralin, and naphthalenes)                                 |
| 30                             | AFG2 | Unknown aromatic fragmentation product #2. (Formed from aromatics containing alkyl groups.)                                  |
| 31                             | -OOH | Chemical operator used to represent reactions at hydroperoxy groups  |
| ACTIVE PRIMARY EMITTED SPECIES |      |  |
| 32                             | ETHE | Ethene   |
| 33+                            | AARn | N'th lumped group used to represent lumped alkanes and/or aromatics. (In general, there will be more than one such species.) |

(continued)

Table 1 (continued) - 2

| No.                                  | Name                    | Description  |
|--------------------------------------|-------------------------|--|
| 34+                                  | OLEn                    | N'th lumped group used to represent lumped higher alkenes. (In general, there will be more than one such species.)   |
| ACTIVE TOTAL PEROXY RADICAL SPECIES  |                         |  |
| 35                                   | RO2.                    | Total alkyl peroxy radicals  |
| 36                                   | RCO3.                   | Total acyl peroxy radicals   |
| PRODUCT ONLY SPECIES                 |                         |  |
| 36                                   | CO2                     | Carbon dioxide   |
| 37                                   | H2SO4                   | Sulphuric acid   |
| 38                                   | H2                      | Hydrogen   |
| 39                                   | -C                      | "Lost carbon." Used to account for carbon balance.   |
| 40                                   | -N                      | "Lost nitrogen." Used to account for nitrogen balance. (Primarily represents C <sub>1</sub> -C <sub>3</sub> organic nitrates, and dinitrophenols, whose reactions are neglected.)                                |
| INORGANIC STEADY STATE SPECIES       |                         |  |
| 41                                   | HO.                     | Hydroxyl radicals  |
| 42                                   | O                       | Ground state oxygen atoms  |
| 43                                   | O*1D2                   | Excited oxygen atoms   |
| STEADY STATE ORGANIC RADICAL SPECIES |                         |  |
| 44                                   | HOCOO.                  | Intermediate formed in the HCHO + HO <sub>2</sub> reaction   |
| 45                                   | CCO-O2.                 | Peroxy acetyl radicals   |
| 46                                   | C2CO-O2.                | Higher acyl peroxy radicals  |
| 47                                   | BZ-CO-O2.               | Peroxy benzoyl radicals  |
| 48                                   | HCOCO-O2.               | Peroxy acyl radical formed from glyoxal  |
| 49                                   | BZ-O.                   | Phenoxy radicals   |
| 50                                   | BZ(NO <sub>2</sub> )-O. | Phenoxy-type radicals containing nitro-groups  |
| STEADY STATE CHEMICAL "OPERATORS"    |                         |  |
| 51                                   | O3OL-SB                 | Chemical operator used to account for the oxidation of SO <sub>2</sub> by ozone - alkene reaction intermediates (This is a product-only species if reactions of SO <sub>2</sub> are removed from the mechanism.) |
| 52                                   | RO2-R.                  | Chemical operator used to represent NO to NO <sub>2</sub> conversion with generation of HO <sub>2</sub> radicals   |
| 53                                   | RO2-X.                  | Chemical operator used to represent NO consumption and alkyl nitrate formation   |

(continued)

Table 1 (continued) - 3

| No.              | Name    | Description  |
|------------------|---------|--|
| 54               | R02-NP. | Chemical operator used to represent NO consumption and nitrophenol formation |
| 55               | R02-XN. | Chemical operator used to represent NO sink reactions                        |
| 56               | R202.   | Chemical operator used to represent extra NO to NO <sub>2</sub> conversions  |
| CONSTANT SPECIES |         |  |
| 57               | O2      | Oxygen   |
| 58               | M       | Air  |
| 59               | HV      | Light factor (1.0 = normal intensity)  |
| 60               | H2O     | Water  |

Table 2. List of Reactions and Rate Constant Parameters for the Detailed Reaction Mechanism, with Comments Giving the Sources of the Rate Parameters and Mechanisms Used

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup>                            | Reaction <sup>c</sup>  |
|---------------------|--|--|
| INORGANIC REACTIONS |  |  |
| 1                   | PHOT=NO2   | $\text{NO}_2 + \text{H}\nu = \text{NO} + \text{O}$   |
|                     |  | Absorption coefficients and quantum yields of NASA (1987) used.<br>(See Table 3 for the absorption coefficients and quantum yields<br>for this and other photolysis reactions in the detailed mechanism) |
| 2                   | 6.0E-34 0.0 -2.3   | $\text{O} + \text{O}_2 + \text{M} = \text{O}_3 + \text{M}$   |
|                     |  | From NASA (1987)   |
| 3A                  | 6.50E-12 -0.238  | $\text{O} + \text{NO}_2 = \text{NO} + \text{O}_2$  |
|                     |  | From NASA (1987)   |
| 3B                  | FALLOFF<br>9.0E-32 0.0 -2.0<br>2.2E-11 0.0 0.0<br>0.6 1.0  | $\text{O} + \text{NO}_2 = \text{NO}_3 + \text{M}$  |
|                     |  | From NASA (1987)   |
| 4                   | 2.00E-12 2.782   | $\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2$  |
|                     |  | From NASA (1987)   |
| 5                   | 1.40E-13 4.968   | $\text{O}_3 + \text{NO}_2 = \text{O}_2 + \text{NO}_3$  |
|                     |  | From NASA (1987)   |
| 6                   | 1.70E-11 -0.298  | $\text{NO} + \text{NO}_3 = \#2 \text{NO}_2$  |
|                     |  | From NASA (1987)   |
| 7                   | 3.30E-39 -1.05   | $\text{NO} + \text{NO} + \text{O}_2 = \#2 \text{NO}_2$   |
|                     |  | Not listed by NASA (1987). Recommendation of Atkinson and Lloyd (1984) used.   |
| 8                   | FALLOFF<br>2.2E-30 0.0 -4.3<br>1.5E-12 0.0 -0.5<br>0.6 1.0 | $\text{NO}_2 + \text{NO}_3 = \text{N}_2\text{O}_5$   |

(continued)

Table 2 (continued) - 2

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>             |
|--|---------------------------------|-----------------------------------|
| From NASA (1987)   |                                 |                                   |
| 9  | 9.09E+26 22.26                  | N2O5 + #RCON8 = NO2 + NO3         |
| The "kinetic parameters" given refer to the equilibrium constant between this reaction and reaction 8. Keq from NASA (1987).   |                                 |                                   |
| 10   | 1.00E-21 0.0                    | N2O5 + H2O = #2 HNO3 ! 298 K only |
| This reaction is assumed to have both a homogeneous and heterogeneous component, based on the results of Tuazon et al. (1983). This reaction represents the "homogeneous" component. The rate constant is derived from the rate of formation of gas phase HNO <sub>3</sub> by Tuazon et al. (1983), and is strictly valid for T=298 K only.  |                                 |                                   |
| 11   | 2.50E-14 2.44                   | NO2 + NO3 = NO + NO2 + O2         |
| Not found in NASA (1987). Rate constant given by Graham and Johnston (1978) used, as recommended by Atkinson and Lloyd (1984).   |                                 |                                   |
| 12A  | PHOT=NO3NO                      | NO3 + HV = NO + O2                |
| 12B  | PHOT=NO3NO2                     | NO3 + HV = NO2 + O                |
| The NO <sub>3</sub> absorption coefficients and quantum yields are based on the evaluation of Carter et al. (1986). The absorption cross sections used are based on the discussion of Atkinson and Lloyd (1984). The quantum yields used are those of Magnotta and Johnston (1980), divided by a factor of 1.5 to yield unit quantum yields at 580-590 nm. [The NASA (1987) recommendations could not be used because they give no absorption coefficients below 600 nm, and make no recommendation for the quantum yields.] |                                 |                                   |
| 13A  | PHOT=O3O3P                      | O3 + HV = O + O2                  |
| The absorption coefficients for 280-320 nm are from Bass and Paur (1984), and those for >320 are those used by Carter et al. (1986). The quantum yields were calculated from those used for the O( <sup>1</sup> D) path, assuming that the total quantum yield is 1.   |                                 |                                   |
| 13B  | PHOT=O3O1D                      | O3 + HV = O*1D2 + O2 ! T = 300 K  |
| The absorption coefficients are from Bass and Paur (1985), and the quantum yields are those recommended by NASA (1987) for T = 300 K. The temperature dependence of the ozone photolysis reaction is ignored in this model.  |                                 |                                   |

(continued)

Table 2 (continued) - 3

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup>  |                   |                      | Reaction <sup>c</sup>                     |
|--------------------|--|-------------------|----------------------|---|
| 14                 | 2.20E-10   | 0.0               |                      | $O^* + D_2 + H_2O = \#2 HO.$              |
|                    | From NASA (1987)   |                   |                      |   |
| 15                 | 1.919E-11  | -0.251            |                      | $O^* + D_2 + M = O + M$                   |
|                    | The rate constants for air are based on $(A, Ea/R) = (1.8E-11, -110)$ for the $N_2$ reaction, and $(A, Ea/R) = (3.2E-11, -70)$ for the $O_2$ reaction (NASA 1987), and assuming $M = 20.95\% O_2$ , with the rest being $N_2$ .  |                   |                      |   |
| 16                 | FALLOFF<br>7.0E-31<br>1.5E-11<br>0.6   | 0.0<br>0.0<br>1.0 | -2.6<br>-0.5<br>-2.6 | $HO. + NO = HONO$                         |
|                    | From NASA (1987)   |                   |                      |   |
| 17                 | PHOT=HONO  |                   |                      | $HONO + HV = HO. + NO$                    |
|                    | The absorption coefficients of Stockwell and Calvert (1978), which are consistent with the recommendation of NASA (1987), are used. Unit quantum yields are assumed.   |                   |                      |   |
| 18                 | FALLOFF<br>2.6E-30<br>2.4E-11<br>0.6   | 0.0<br>0.0<br>1.0 | -3.2<br>-1.3<br>-3.2 | $HO. + NO_2 = HNO_3$                      |
|                    | From NASA (1987)   |                   |                      |   |
| 19                 | 6.45E-15   | -1.652            |                      | $HO. + HNO_3 = H_2O + NO_3$ ! 1 ATM ONLY. |
|                    | The rate constants were calculated for 1 atm and $T = 270, 300$ , and $330\text{ K}$ , using the expression given by NASA (1987), and then $A$ and $Ea$ were calculated for using least squares. This rate constant expression is thus valid for one atmosphere pressure only. |                   |                      |   |
| 20                 | (ignored)  |                   |                      | $HNO_3 + HV = HO. + NO_2$                 |
|                    | The photolysis of nitric acid is ignored in this model.  |                   |                      |   |
| 21                 | 2.40E-13   | 0.0               |                      | $HO. + CO = HO_2. + CO_2$ ! 1 ATM ONLY    |

(continued)

Table 2 (continued) - 4

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup>  |                   |                     | Reaction <sup>c</sup>  |
|--|--|-------------------|---------------------|--|
| The rate constant for one atmosphere pressure was calculated using the expression given by NASA (1987). The temperature dependence is assumed to be small. |  |                   |                     |  |
| 22   | 1.60E-12   | 1.87              |                     | $\text{HO}_\cdot + \text{O}_3 = \text{HO}_2\cdot + \text{O}_2$   |
|  | From NASA (1987)   |                   |                     |  |
| 23   | 3.70E-12   | -0.48             |                     | $\text{HO}_2\cdot + \text{NO} = \text{HO}_\cdot + \text{NO}_2$   |
|  | From NASA (1987)   |                   |                     |  |
| 24   | FALLOFF<br>1.8E-31<br>4.7E-12<br>0.6   | 0.0<br>0.0<br>1.0 | -3.2<br>-1.4<br>1.0 | $\text{HO}_2\cdot + \text{NO}_2 = \text{HNO}_4$  |
|  | From NASA (1987)   |                   |                     |  |
| 25   | 4.76E+26   | 21.66             |                     | $\text{HNO}_4 + \#RCON24 = \text{HO}_2\cdot + \text{NO}_2$   |
|  | The "kinetic parameters" refer to the equilibrium constant between this reaction and reaction 24. The Keq is from NASA (1987). |                   |                     |  |
| 26   | (ignored)  |                   |                     | $\text{HNO}_4 + \text{HV} = \text{products}$   |
|  | This reaction is ignored in this model.  |                   |                     |  |
| 27   | 1.30E-12   | -0.755            |                     | $\text{HNO}_4 + \text{HO}_\cdot = \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$                                   |
|  | From NASA (1987)   |                   |                     |  |
| 28   | 1.10E-14   | 0.994             |                     | $\text{HO}_2\cdot + \text{O}_3 = \text{HO}_\cdot + \#2 \text{ O}_2$  |
|  | From NASA (1987)   |                   |                     |  |
| 29A  | 2.20E-13   | -1.23             |                     | $\text{HO}_2\cdot + \text{HO}_2\cdot = \text{HO}_2\text{H} + \text{O}_2$   |
| 29B  | 1.90E-33   | -1.95             |                     | $\text{HO}_2\cdot + \text{HO}_2\cdot + \text{M} = \text{HO}_2\text{H} + \text{O}_2$                                |
| 29C  | 3.10E-34   | -5.60             |                     | $\text{HO}_2\cdot + \text{HO}_2\cdot + \text{H}_2\text{O} = \text{HO}_2\text{H} + \text{O}_2 + \text{H}_2\text{O}$ |
| 29D  | 6.60E-35   | -6.32             |                     | $\text{HO}_2\cdot + \text{HO}_2\cdot + \text{H}_2\text{O} = \text{HO}_2\text{H} + \text{O}_2 + \text{H}_2\text{O}$ |
|  | (1 ATM ONLY)   |                   |                     |  |

The temperature, pressure, and  $\text{H}_2\text{O}$  dependence used for this reaction is based on the data of Kircher and Sander (1984), as discussed by Carter et al. (1986). [NASA (1987) does not give

(continued)

Table 2 (continued) - 5

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>   |
|--|---------------------------------|---|
| H <sub>2</sub> O-dependencies.] Reaction 29D is based on (A, Ea) = (2.7E-54, -6.32) for HO <sub>2</sub> . + HO <sub>2</sub> . + M + H <sub>2</sub> O, but the software cannot process reactions with four reactants, so the reaction as written above is valid for one atmosphere pressure only. |                                 |   |
| 30A  | SAMEK 29A                       | NO <sub>3</sub> + HO <sub>2</sub> . = HNO <sub>3</sub> + O <sub>2</sub>   |
| 30B  | SAMEK 29B                       | NO <sub>3</sub> + HO <sub>2</sub> . + M = HNO <sub>3</sub> + O <sub>2</sub>   |
| 30C  | SAMEK 29C                       | NO <sub>3</sub> + HO <sub>2</sub> . + H <sub>2</sub> O = HNO <sub>3</sub> + O <sub>2</sub> + H <sub>2</sub> O                 |
| 30A  | SAMEK 29D                       | NO <sub>3</sub> + HO <sub>2</sub> . + H <sub>2</sub> O = HNO <sub>3</sub> + O <sub>2</sub> + H <sub>2</sub> O<br>(1 ATM ONLY) |

Assumed to have same rate constant and pressure and H<sub>2</sub>O dependencies as the HO<sub>2</sub> + HO<sub>2</sub>. reaction.

#### REACTIONS OF H<sub>2</sub>O<sub>2</sub>

(The following three reactions can be removed from airshed model applications where predictions of H<sub>2</sub>O<sub>2</sub> are not important. They have no significant effect on predictions of ozone formation.)



Absorption cross section based on NASA (1988) recommendation.  
Unit quantum yields assumed.



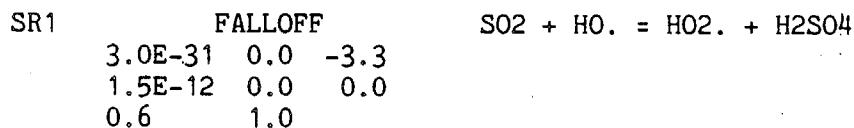
From NASA (1987)



From NASA (1987). (This reaction was added because it affects predictions of H<sub>2</sub>O<sub>2</sub>. It has no significant effect on ozone.)

#### REACTIONS OF SO<sub>2</sub>

(The following reactions are only needed for airshed model applications where predictions of SO<sub>2</sub> and sulfate are of interest.)



(continued)

Table 2 (continued) - 6

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>                                      |
|---|---------------------------------|--|
| From NASA (1988)  |                                 |  |
| SR2   | 2.30E-17                        | O3OL-SB + H <sub>2</sub> O =                               |
| SR3   | 1.00E-13                        | O3OL-SB + SO <sub>2</sub> = H <sub>2</sub> SO <sub>4</sub> |
| <p>The chemical operator O3OL-SB is used to account for the oxidation of SO<sub>2</sub> by stabilized Criegee biradicals formed in the ozone + alkene reactions. This zero-carbon pseudo-species is formed in the mechanism whenever Criegee biradicals are stabilized. The rate constants for its reactions (with H<sub>2</sub>O and SO<sub>2</sub>) are based on those recommended by Atkinson (1988) for Criegee biradicals. The rate constant for the SO<sub>2</sub> reaction is unknown, and the arbitrary value assumed by Carter et al. (1986) is used. The rate constant for the H<sub>2</sub>O reaction is based on k(CH<sub>2</sub>O<sub>2</sub>. + H<sub>2</sub>O)/k(CH<sub>2</sub>O<sub>2</sub>. + SO<sub>2</sub>) = 2.3E-4, from Suto et al. (1985), as given by Atkinson (1988). Atkinson (1988) recommends that the reactions of Criegee biradicals with NO and NO<sub>2</sub> can be neglected.</p> |                                 |  |

## REACTIONS OF FORMALDEHYDE

|    |               |                                       |
|----|---------------|---------------------------------------|
| C1 | PHOT=HCHOAVGR | HCHO + HV = #2 HO <sub>2</sub> . + CO |
| C2 | PHOT=HCHOAVGM | HCHO + HV = H <sub>2</sub> + CO       |

The formaldehyde cross section values were derived by averaging 1 nm values derived by Jeffries (private communication, 1988) from the data of Bass et al. (1980) and Moortgat et al. (1983). Averaging these data is recommended by NASA (1987), but the data tabulated there lack adequate resolution.

The quantum yields are derived from those tabulated in NASA (1987) in 10 nm intervals. Data between 10 nm intervals were obtained by interpolating the tabulated 10 nm average values.

The absorption coefficient and quantum yields for all photolysis reactions are given in Table 3.

|    |          |       |  |
|----|----------|-------|--|
| C3 | 1.60E-11 | 0.219 | HCHO + HO <sub>2</sub> . = HO <sub>2</sub> . + CO + H <sub>2</sub> O |
|----|----------|-------|--|

Atkinson (1988) recommendation.

|     |          |       |  |
|-----|----------|-------|--|
| C4  | 1.10E-13 | 0.000 | HCHO + HO <sub>2</sub> . = HO <sub>2</sub> O <sub>2</sub> .                      |
| C4A | 2.00E+01 |       | HO <sub>2</sub> O <sub>2</sub> . = HO <sub>2</sub> . + HCHO                      |
| C4B | SAMEK B1 |       | HO <sub>2</sub> O <sub>2</sub> . + NO = -C + NO <sub>2</sub> + HO <sub>2</sub> . |

(continued)

Table 2 (continued) - 7

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>   |
|---|---------------------------------|---|
| The mechanism and rate constants used for the HCHO + HO <sub>2</sub> reactions are those recommended by Atkinson (1988). This is based on data of Barnes et al. (1985).   |                                 |   |
| The reactions of formic acid expected to be formed in the above reactions are ignored. -C is given as the product to indicate that the carbon in formic acid is "lost."   |                                 |   |
| Note that the rate constant for reaction C4B is assumed to be the same as used for other peroxy radical + NO reactions in the mechanism, as is given below.   |                                 |   |
| C9  | 2.80E-12    5.00                | HCHO + NO <sub>3</sub> = HNO <sub>3</sub> + HO <sub>2</sub> . + CO                                  |
| The Arrhenius parameters for this reaction were derived based on the NASA (1987) recommendation of k = 6.0E-16 for T = 298 K, and an estimated A of 2.8E-12, which is 2 x the A for NO <sub>3</sub> + acetaldehyde recommended by Atkinson (1988).  |                                 |   |
| REACTIONS OF ACETALDEHYDE AND PAN   |                                 |   |
| C10   | 5.60E-12    -0.616              | CCHO + HO. = CCO-O <sub>2</sub> . + H <sub>2</sub> O + RC <sub>2</sub> O <sub>3</sub> .             |
| Rate constant recommended by Atkinson (1988). (Note that the formation of the operator "RC <sub>2</sub> O <sub>3</sub> ." as the product is used to account for the contribution of acetyl peroxy radical formation to the total acyl peroxy radical levels. See listing of "lumped peroxy radical reactions," below.)  |                                 |   |
| C11A  | PHOT=CCHOR                      | CCHO + HV = CO + HO <sub>2</sub> . + HCHO + RO <sub>2</sub> -R. + RO <sub>2</sub> .                 |
| C11B  | (ignored)                       | CCHO + HV = CH <sub>4</sub> + CO  |
| Absorption coefficients and quantum yields are those recommended by Baulch et al. (1984). The photolysis route forming molecular products has no significant effect on model predictions and is ignored. (Note that the set of products HCHO + RO <sub>2</sub> -R. represent the net effects of the formation of methyl peroxy radicals, and that the formation of the operator "RO <sub>2</sub> ." is used to account for the contribution of methyl peroxy radical formation to total alkyl peroxy radical levels.) |                                 |   |
| C12   | 1.40E-12    3.696               | CCHO + NO <sub>3</sub> = HNO <sub>3</sub> + CCO-O <sub>2</sub> . + RC <sub>2</sub> O <sub>3</sub> . |

(continued)

Table 2. (continued) - 8

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup>                                    | Reaction <sup>c</sup>  |
|---|--|--|
| Kinetic parameters recommended by Atkinson (1988).  |  |  |
| C13   | SAMEK B2   | $\text{CCO-O}_2\cdot + \text{NO} = \text{CO}_2 + \text{NO}_2 + \text{HCHO} + \text{RO}_2\text{-R.}$<br>$+ \text{RO}_2.$              |
| C14   | SAMEK B4   | $\text{CCO-O}_2\cdot + \text{NO}_2 = \text{PAN}$   |
| C15   | SAMEK B6   | $\text{CCO-O}_2\cdot + \text{HO}_2\cdot = -\text{OOH} + \text{CO}_2 + \text{HCHO}$   |
| C16   | SAMEK B9   | $\text{CCO-O}_2\cdot + \text{RO}_2\cdot = \text{RO}_2\cdot + .5 \text{HO}_2\cdot + \text{CO}_2$<br>$+ \text{HCHO}$                   |
| C17   | SAMEK B10  | $\text{CCO-O}_2\cdot + \text{RCO}_3\cdot = \text{RCO}_3\cdot + \text{HO}_2\cdot + \text{CO}_2 + \text{HCHO}$                         |
| These are assumed to have the same rate constants as used for the lumped peroxy radical species $\text{RCO}_3\cdot$ , whose reactions are given below.  |  |  |
| C18   | FALLOFF<br>6.17E-02 25.402 0.0<br>2.20E+16 26.702 0.0<br>0.27 1.47 | $\text{PAN} = \text{CCO-O}_2\cdot + \text{NO}_2 + \text{RCO}_3\cdot$   |
| Rate constant expression recommended by Atkinson (1988), based on data of Reimer and Zabel (1986) for $M=N_2$ , calculated for $M=air$ , using $k_0(O_2)/k_0(N_2) = 0.9$ , as tabulated by Atkinson (1988). |  |  |
| REACTIONS OF PROPIONALDEHYDE AND PPN (ALSO USED FOR LUMPED HIGHER ALDEHYDES AND LUMPED HIGHER ACYL PEROXY NITRATES)   |  |  |
| C25   | 8.50E-12 -0.50   | $\text{RCHO} + \text{HO}\cdot = \text{C}_2\text{CO-O}_2\cdot + \text{RCO}_3\cdot$  |
| Rate constant for $T=298$ K recommended by Atkinson (1988). Temperature dependence estimated by Carter et al. (1986) assumed.   |  |  |
| C26   | PHOT=RCHO  | $\text{RCHO} + \text{HV} = \text{CCHO} + \text{RO}_2\text{-R.} + \text{RO}_2\cdot + \text{CO} + \text{HO}_2$                         |
| The absorption coefficients used are from Calvert and Pitts (1966). The quantum yields based on the data of Heicklen et al. (1986).   |  |  |
| C27   | 1.40E-12 3.696   | $\text{NO}_3 + \text{RCHO} = \text{HN}_3 + \text{C}_2\text{CO-O}_2\cdot + \text{RCO}_3\cdot$   |
| Assumed to react with the same kinetics as used for $\text{NO}_3 +$ acetaldehyde.   |  |  |
| C28   | SAMEK B2   | $\text{C}_2\text{CO-O}_2\cdot + \text{NO} = \text{CCHO} + \text{RO}_2\text{-R.} + \text{CO}_2 + \text{NO}_2$<br>$+ \text{RO}_2\cdot$ |
| C29   | 5.95E-12 0.0 -3.6  | $\text{C}_2\text{CO-O}_2\cdot + \text{NO}_2 = \text{PPN}$  |

(continued)

Table 2 (continued) - 9

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|--------------------|---------------------------------|--|
| C30                | SAMEK B6                        | $\text{C}_2\text{CO}-\text{O}_2 + \text{HO}_2 = \text{-OOH} + \text{CCHO} + \text{CO}_2$   |
| C31                | SAMEK B9                        | $\text{C}_2\text{CO}-\text{O}_2 + \text{RO}_2 = \text{RO}_2 + .5 \text{HO}_2 + \text{CCHO}$<br>+ $\text{CO}_2$   |
| C32                | SAMEK B10                       | $\text{C}_2\text{CO}-\text{O}_2 + \text{RCO}_3 = \text{RCO}_3 + \text{HO}_2 + \text{CCHO} + \text{CO}_2$   |
|                    |                                 | The high pressure limit recommended by Atkinson (1988) for the acetyl peroxy + $\text{NO}_2$ rate constant, is used for the corresponding reaction of propionyl peroxy radicals. The other rate constants are the same as used for the lumped acyl peroxy radical, $\text{RCO}_3$ , which are given below. Note that using different rate constants for the $\text{NO}_2$ reactions of the $\text{RCO}_3$ 's results in a slight inaccuracy in the calculation of the total $\text{RCO}_3$ levels. However, this should be minor, especially if most of the $\text{RCO}_3$ is $\text{CCO-O}_2$ . |
| C33                | 1.60E+17 27.966                 | $\text{PPN} = \text{C}_2\text{CO}-\text{O}_2 + \text{NO}_2 + \text{RCO}_3$ .   |
|                    |                                 | Kinetic parameters recommended by Atkinson (1988).   |
|                    |                                 | REACTIONS OF ACETONE   |
| C38                | 1.70E-12 1.192                  | $\text{ACET} + \text{HO} = .8 \text{"MGLY} + \text{RO}_2-\text{R."}$<br>+ $.2 \text{"R2O}_2 + \text{HCHO} + \text{CCO-O}_2$ .<br>+ $\text{RCO}_3$ " + $\text{RO}_2$ .  |
|                    |                                 | Kinetic parameters recommended by Atkinson (1988). Mechanism is based on $\text{CH}_3-\text{CO-CH}_2-\text{O}$ . branching ratio estimates given by Atkinson (1988).   |
| C39                | PHOT=ACETONE                    | $\text{ACET} + \text{HV} = \text{CCO-O}_2 + \text{HCHO} + \text{RO}_2-\text{R.} + \text{RCO}_3$ .<br>+ $\text{RO}_2$ .   |
|                    |                                 | The absorption coefficients for acetone were taken from the data base developed for the RADM model (NCAR 1987), provided by Stockwell (1988). They are consistent with the values tabulated in Calvert and Pitts (1966). The quantum yields are based on those of Meyrahn et al. (1986), as recommended by Atkinson (1988).  |
|                    |                                 | REACTIONS OF METHYL ETHYL KETONE AND LUMPED HIGHER KETONES   |
| C44                | 2.30E-12 0.338                  | $\text{MEK} + \text{HO} = \text{H}_2\text{O} + .5 \text{"CCHO} + \text{HCHO}$<br>+ $\text{CCO-O}_2 + \text{C}_2\text{CO}-\text{O}_2$ " + $\text{RCO}_3$ .<br>+ $1.5 \text{"R2O}_2 + \text{RO}_2$ "   |
|                    |                                 | Kinetic parameters constant recommended by Atkinson (1988), based on data of Wallington and Kurylo (1987). The mechanism used is that assumed by Carter et al. (1986).   |

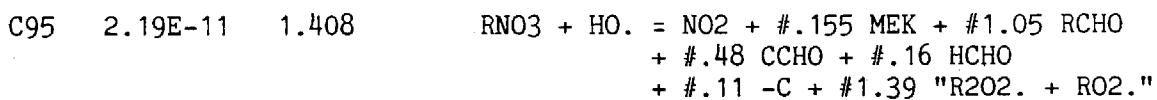
(continued)

Table 2 (continued) - 10

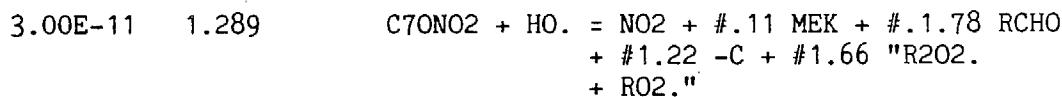
| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>                                      |
|--------------------|---------------------------------|--|
| C57 PHOT=KETONE    |                                 | MEK + HV + #.1 = CCO-02. + CCHO + RO2-R.<br>+ RC03. + RO2. |

The absorption coefficients used for MEK are from Calvert and Pitts (1966). The overall MEK quantum yield of 0.1 was derived based on fits to UNC chamber data as determined by Carter et al. (1986).

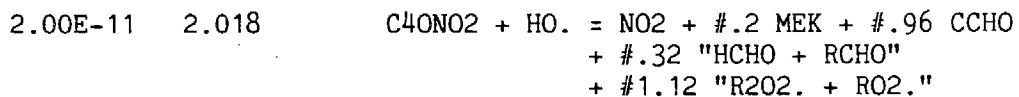
## REACTIONS OF THE LUMPED ALKYL NITRATE



The above consists of the average of the reactions of the lumped C<sub>4</sub> nitrate and the lumped C<sub>7</sub> nitrate used in the mechanism of Carter et al. (1986). These are as follows:

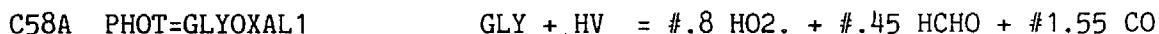


and

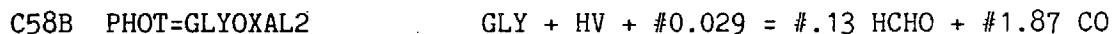


The Arrhenius parameters were determined from their calculated rate constants at 270, 300, and 330 K. Note that this species is represented as having 5 carbons, not 5.5 as would be the case for the average of C<sub>4</sub>ONO<sub>2</sub> and C<sub>7</sub>ONO<sub>2</sub>.

## REACTIONS OF GLYOXAL AND ITS PAN ANALOGUE



This reaction refers to photolysis at the low wavelength band. The quantum yields are based on data of Langford and Moore (1984), and references therein. The absorption coefficients are from Plum et al. (1983). Note that the data of Plum et al. give no information on quantum yields in this low wavelength band, since the light source they used had no intensity in this wavelength region.



(continued)

Table 2 (continued) - 11

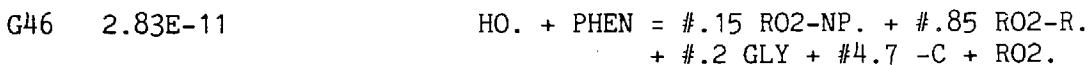
| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|---|---------------------------------|--|
| This reaction refers to photolysis at the high wavelength band. The quantum yields and absorption coefficients are from Plum et al. (1983).   |                                 |  |
| C59   | 1.12E-11                        | GLY + HO. = #.6 HO2. + #1.2 CO<br>+ #.4 "HCOCO-O2. + RC03."        |
| Rate constant of Plum et al. (1983), as tabulated by Atkinson (1986), used. Product yields based on discussion of Atkinson (1988).  |                                 |  |
| C60   | SAMEK C12                       | GLY + NO3 = HNO3 + #.6 HO2. + #1.2 CO<br>+ #.4 "HCOCO-O2. + RC03." |
| Assumed to have the same kinetics as NO <sub>3</sub> + acetaldehyde. Assumed to have an analogous mechanism as the OH radical reaction.   |                                 |  |
| C62   | SAMEK B2                        | HCOCO-O2. + NO = NO2 + CO2 + CO + HO2.                             |
| C63   | SAMEK B4                        | HCOCO-O2. + NO2 = GPAN   |
| C65   | SAMEK B6                        | HCOCO-O2. + HO2. = -OOH + CO2 + CO                                 |
| C66   | SAMEK B9                        | HCOCO-O2. + RO2. = RO2. + #.5 HO2. + CO2<br>+ CO                   |
| C67   | SAMEK B10                       | HCOCO-O2. + RC03. = RC03. + HO2. + CO2 + CO                        |
| These are assumed to have the same kinetics as the analogous reactions of CCO-O <sub>2</sub> . and RC0 <sub>3</sub> .   |                                 |  |
| C64   | SAMEK C18                       | GPAN = HCOCO-O2. + NO2 + RC03.                                     |
| This is assumed to have the same kinetics as the decomposition of PAN.  |                                 |  |
| REACTIONS OF METHYL GLYOXAL   |                                 |  |
| C68A  | PHOT=MEGLYOX1                   | MGLY + HV = HO2. + CO + CCO-O2. + RC03.                            |
| This reaction represents photolysis at the low wavelength region. Quantum yields are assumed to be unity by analogy with photolysis of glyoxal at the low wavelength region. Absorption coefficients are from Plum et al. (1983). |                                 |  |
| C68B  | PHOT=MEGLYOX2                   | MGLY + HV + #.107 = HO2. + CO + CCO-O2.<br>+ RC03.                 |

(continued)

Table 2 (continued) - 12

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|--------------------|---------------------------------|--|
|                    |                                 | This reaction represents photolysis at the high wavelength region. Quantum yields and absorption coefficients are based on the data of Plum et al. (1983).                 |
| C69                | 1.69E-11                        | $\text{MGLY} + \text{HO.} = \text{CO} + \text{CCO-O}_2 + \text{RCO}_3$ .   |
|                    |                                 | Rate constant based on data of Plum et al (1983). The initially formed $\text{CH}_3\text{-CO-CO}_2$ radical is estimated to decompose rapidly to the products shown above. |
| C70                | SAMEK C12                       | $\text{MGLY} + \text{NO}_3 = \text{HNO}_3 + \text{CO} + \text{CCO-O}_2 + \text{RCO}_3$ .   |
|                    |                                 | This reaction is assumed to have the same kinetics as the reaction of $\text{NO}_3$ with acetaldehyde.   |

## REACTIONS OF PHENOL

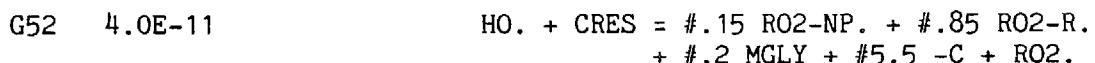


Rate constant of Rinke and Zetzel (1984), tabulated by Atkinson (1986), is assumed. The mechanism is assumed to be analogous to the empirical mechanism derived for o-cresol, shown below.



Rate constant recommended by Atkinson (1988). Phenoxy radical reactions are shown below with the reactions of nitrophenols.

## REACTION OF CRESOLS AND OTHER ALKYLPHENOLS



The rate constant used is that recommended by Atkinson (1988) for o-cresol.

The mechanism for the reaction of OH radicals with phenolic compounds is unknown, and is not represented explicitly. In order to fit the data from the o-cresol- $\text{NO}_x$ -air run EC-281 it is assumed to proceed via a radical-propagating and radical-terminating path, with the amount of termination being adjusted to be 0.15 in order to fit the reactivity observed in that run.

In addition, assuming a methylglyoxal yield of 0.8 allows the PAN yields observed in that run to be fit. Reactions of other products

(continued)

Table 2 (continued) - 13

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|---|---------------------------------|--|
| <p>formed are neglected. [The adjustment was done using the version of the mechanism given in Lurmann et al. (1987a). These parameters may not be optimum for this version of the mechanism, but were not re-adjusted. The mechanism assumed for this reaction has only a minor effect on model predictions, because under most conditions consumption of phenolic compounds by reaction with NO<sub>3</sub> radicals dominates.]</p>   |                                 |  |
| G57   | 2.1E-11                         | $\text{NO}_3 + \text{CRES} = \text{HN}O_3 + \text{BZ-O.} + -\text{C}$                                  |
| <p>Rate constant recommended by Atkinson (1988) for o-cresol.</p>   |                                 |  |
| <p>REACTIONS OF BENZALDEHYDE, PBzN AND ANALOGOUS AROMATIC COMPOUNDS</p>   |                                 |  |
| G30   | 1.3E-11                         | $\text{BALD} + \text{HO.} = \text{BZ-CO-O2.} + \text{RCO3.}$   |
| <p>Rate constant recommended by Atkinson (1986).</p>  |                                 |  |
| G31   | PHOT=BZCHO                      | $\text{BALD} + \text{HV} + \# .05 = \# 7 -\text{C}$  |
| <p>Absorption coefficients from the data of Majer et al. (1969) for benzaldehyde in n-hexane. They must be considered to be only qualitative in nature. The overall quantum yield of 0.05 was adjusted to fit the benzaldehyde consumption rate observed in toluene + benzaldehyde runs EC-337 and EC-339. The quantum yield is assumed to be independent of wavelength, because no data concerning its wavelength dependence are available. The products formed from benzaldehyde photolysis are unknown, except that both radical formation and benzene formation appear to be minor. Thus, it is assumed that the benzaldehyde photooxidation products are unreactive.</p> |                                 |  |
| G32   | 1.40E-12    3.747               | $\text{BALD} + \text{NO}_3 = \text{HN}O_3 + \text{BZ-CO-O2.}$  |
| <p>Kinetics estimated based on 298 K rate constant recommended by Atkinson (1988), and assuming the A factor is the same as for the reaction of NO<sub>3</sub> + acetaldehyde.</p>  |                                 |  |
| G33   | SAMEK B2                        | $\text{BZ-CO-O2.} + \text{NO} = \text{BZ-O.} + \text{CO}_2 + \text{NO}_2 + \text{R2O2.} + \text{RO2.}$ |
| G36   | SAMEK B6                        | $\text{BZ-CO-O2.} + \text{HO2.} = -\text{OOH} + \text{CO}_2 + \text{PHEN}$                             |
| G34   | 5.95E-12    0.0    -3.6         | $\text{BZ-CO-O2.} + \text{NO2} = \text{PBZN}$  |
| G37   | SAMEK B9                        | $\text{BZ-CO-O2.} + \text{RO2.} = \text{RO2.} + \# .5 \text{ HO2.} + \text{CO}_2 + \text{PHEN}$        |

(continued)

Table 2 (continued) - 14

| Label <sup>a</sup>                             | Kinetic Parameters <sup>b</sup> |        | Reaction <sup>c</sup>   |
|--|---------------------------------|--------|---|
| G38  | SAMEK B10                       |        | BZ-CO-O2. + RCO3. = RCO3. + HO2. + CO2 + PHEN   |
|  |                                 |        | The high pressure limit for CCO-O2. (RCO3.) + NO2 is used for the corresponding reaction of BZ-CO-O2. The other rate constants are the same as for CCO-O2. Note that using different k's for the NO2 reactions of the RCO3's results in a slight inaccuracy in the calculation of the total RCO3 levels. However, this should be minor, especially if most of the RCO3 is CCO-O2.                   |
| G35  | 1.60E+15                        | 25.90  | PBNZ = BZ-CO-O2. + NO2 + RCO3.  |
|  |                                 |        | Rate expression based on data of Kenley and Hendry (1982).  |
| REACTIONS OF PHENOXY RADICALS AND NITROPHENOLS |                                 |        |   |
| G43  | 1.5E-11                         |        | BZ-O. + NO2 = NPHE  |
|  |                                 |        | This is assumed to react with a similar rate constant as recommended by Atkinson (1988) methoxy + NO2.  |
| G44  | 1.75E-13                        | -1.987 | BZ-O. + HO2. = PHEN   |
|  |                                 |        | This is assumed to react with the same rate constant as used for peroxy + HO2 reactions (see below), and to form phenol + O2.   |
| G45  | 1.0E-3                          |        | BZ-O. = PHEN  |
|  |                                 |        | This reaction is included to avoid problems if BZ-O. is ever formed under conditions where HO2 and NO2 are very low (which is considered to be unlikely under most reasonable conditions), and can be considered to represent its reaction with organics present. The rate constant is arbitrary, and is such that this process becomes significant only if [NO2] < ~3E-6 ppm and [HO2] < 1E-5 ppm. |
| G58  | 3.60E-12                        |        | NPHE + NO3 = HNO3 + BZ(NO2)-O.  |
|  |                                 |        | This reaction is assumed to have the same rate constant as the analogous reaction of phenol. Reaction of nitrophenols with NO3 is assumed to dominate over reaction with OH radicals, so the latter is ignored.   |
| G59  | 1.50E-11                        |        | BZ(NO2)-O. + NO2 = #2 -N + #6 -C  |
| G60  | 1.75E-13                        | -1.987 | BZ(NO2)-O. + HO2. = NPHE  |
| G61  | 1.00E-3                         |        | BZ(NO2)-O. = NPHE   |

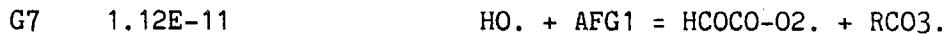
(continued)

Table 2 (continued) - 15

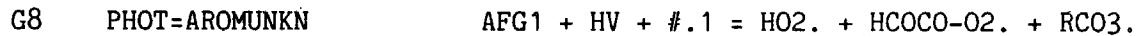
| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup> |
|--|---------------------------------|-----------------------|
| These reactions are assumed to be analogous to the corresponding reactions of phenoxy radicals (BZ-0.), above. The di-nitro compound formed in reaction G59 is assumed to condense into the aerosol phase, and thus its gas phase reactions are ignored. |                                 |                       |

REACTIONS OF THE UNCHARACTERIZED AROMATIC RING-OPENING PRODUCT #1

(This pseudo-species is used to represent the contribution of uncharacterized aromatic ring-opening products to the overall reactivity of benzene, naphthalene, and other aromatics which do not have alkyl groups. Its reactions are assumed to be like glyoxal, except that it photolyzes more rapidly to form radicals, and photolyzes primarily at lower wavelengths. Its yield in the reactions of the parent compound are adjusted to fit overall reactivity observed in the aromatic-NO<sub>x</sub>-air runs.)



Assumed to have the same rate constant as used for glyoxal. The mechanism is essentially arbitrary, but formation of a PAN analogue tends to result in somewhat better predictions of maximum ozone yields in aromatic systems, and is analogous to what is assumed for uncharacterized ring fragmentation products in other mechanisms. The glyoxal PAN analogue is used to avoid the predicted formation of PAN in systems where no alkyl groups are present.



The rate of this photolysis is essentially arbitrary, though it is assumed to be rapid to simulate results of benzene-NO<sub>x</sub>-air irradiations. It is arbitrarily assumed to be 10 times slower than the analogous photolysis of AFG2, the alkyl-containing uncharacterized aromatic ring fragmentation product. The spectral response for the photolysis of these pseudo-species is adjusted so the same mechanism can fit the results of aromatic-NO<sub>x</sub>-air runs carried out in the SAPRC ITC with blacklight irradiation as in the SAPRC EC, with solar simulator irradiation. See Carter et al. (1987).

REACTIONS OF THE UNCHARACTERIZED AROMATIC RING-OPENING PRODUCT #2

(This pseudo-species is used to represent the contribution of uncharacterized aromatic ring-opening products to the overall reactivity of toluene, xylenes, alkyl naphthalenes, and other aromatic compounds with alkyl side-groups. Its reactions are

(continued)

Table 2 (continued) - 16

| Label <sup>a</sup>                          | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>   |
|---|---------------------------------|---|
|   |                                 | assumed to be like methyl glyoxal, except that it photolyzes more rapidly, and primarily at lower wavelengths. Its yield in the reactions of the parent compound are adjusted to fit overall reactivity observed in the aromatic-NO <sub>x</sub> -air runs.)  |
| G9  | 1.69E-11                        | $\text{HO}_\cdot + \text{AFG2} = \text{C}_2\text{CO}-\text{O}_2\cdot + \text{RCO}_3$ .  |
|   |                                 | The rate constant for the corresponding reaction of methyl glyoxal is used. PPN is used to represent the PAN analogues which are assumed to be formed from these uncharacterized products. This is consistent with the use of PPN to represent all the higher PAN analogues, other than those which are explicitly represented.   |
| G10   | PHOT=AROMUNKN                   | $\text{AFG2} + \text{HV} = \text{HO}_2\cdot + \text{CO} + \text{CCO}-\text{O}_2\cdot + \text{RCO}_3$ .  |
|   |                                 | The photolysis rate of this reaction is essentially arbitrary, except that it must be assumed to be rapid to fit the results of aromatic-NO <sub>x</sub> -air irradiations carried out in the SAPRC ITC, and that the spectral response of the photolysis reaction is derived from simulations of runs carried out in the SAPRC EC and ITC, as discussed above for AFG1. It is assumed to have the same mechanism as the photolysis of methyl glyoxal.  |
| REACTIONS OF THE LUMPED HYDROPEROXIDE GROUP |                                 |   |
|   |                                 | [This mechanism does not represent the reactions of the organic hydroperoxides formed in peroxy + HO <sub>2</sub> reactions separately, but instead represents them, in effect, by the same set of organic species which would be formed if their precursor peroxy radicals reacted with NO, plus the zero-carbon lumped structure group "-OOH." The latter is used to represent the effects of radical generation caused by photolysis at this group, and the radical and NO <sub>x</sub> conversion effects caused by OH reaction at this group. See Carter et al. (1986) for a discussion of this hydroperoxide lumping approach.] |
| B7  | PHOT=CO2H                       | $-\text{OOH} + \text{HV} = \text{HO}_2\cdot + \text{HO}_\cdot$ .  |
|   |                                 | The absorption coefficients used for the lumped hydroperoxide group are those measured by Molina and Arguello (1979) for methyl hydroperoxide, as recommended by NASA (1988). Quantum yields of unity are assumed.  |

(continued)

Table 2 (continued) - 17

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|---|---------------------------------|--|
| B7A   | 5.0E-12                         | $\text{HO}_\cdot + \text{-OOH} = \text{HO}$ .                                |
| B7B   | 5.0E-12                         | $\text{HO}_\cdot + \text{-OOH} = \text{RO}_2\text{-R}_\cdot + \text{RO}_2$ . |
| <p>The rate constant for the reactions of OH radicals at the hydroperoxide group are based on data of Niki et al. (1983) for methyl hydroperoxide, as discussed by Atkinson (1986). The branching ratio is assumed to be 50/50 for general hydroperoxides, based also on the data of Niki et al. for methyl hydroperoxide. Reaction B7A represents the process where OH abstracts from the carbon alpha to the -OOH group, which is followed by formation of OH and the corresponding carbonyl (e.g.,</p> $\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_2\text{OOH}$ $\cdot\text{CH}_2\text{OOH} \rightarrow \text{HCHO} + \text{OH}$  |                                 |  |
| <p>Reaction B7B represents the process where OH abstracts from the -OOH group, resulting in the formation of the corresponding peroxide. Reaction at other sites are ignored, since the -OOH group is probably preserved in those cases, and these reactions are represented by the reactions of the species used to represent the carbon-containing portion of the hydroperoxide.</p>  |                                 |  |
| <h4>LUMPED ALKYL AND ACYL PEROXY RADICAL REACTIONS</h4> <p>(The operators <math>\text{RO}_2\cdot</math> and <math>\text{RCO}_3\cdot</math> are active species which are used to represent the total peroxy radical concentrations, for the purpose of determining branching ratios for <math>\text{RO}_2/\text{RCO}_3 + \text{NO}</math>, <math>\text{NO}_2</math>, <math>\text{HO}_2</math>, or peroxy reactions. In order to be used properly, each reaction which forms an alkylperoxy radical should form an equal amount of "<math>\text{RO}_2\cdot</math>," and likewise for acylperoxy radicals and "<math>\text{RCO}_3\cdot</math>." In addition, the rate constants for their reactions with <math>\text{NO}</math>, <math>\text{NO}_2</math>, <math>\text{HO}_2\cdot</math>, <math>\text{RO}_2\cdot</math>, and <math>\text{RCO}_3\cdot</math> should have the same rate constants as used for the corresponding reactions below. Note that these operators have no mass and are not radicals; they are just used for the calculation of branching ratios. Thus, these "reactions" have no effect on any species other than <math>\text{RO}_2\cdot</math> or <math>\text{RCO}_3\cdot</math> themselves. These must be treated as active species in the model calculation, or the model will not operate properly under <math>\text{NO}_x</math>-free or light-free conditions.)</p> |                                 |  |
| B1  | 4.20E-12                        | $\text{RO}_2\cdot + \text{NO} = \text{NO}$                                   |
| B2  | 4.20E-12                        | $\text{RCO}_3\cdot + \text{NO} = \text{NO}$                                  |

The kinetics of these reactions are based on the recommendation of Atkinson (1988).

(continued)

Table 2 (continued) - 18

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup>                               | Reaction <sup>c</sup>  |
|--------------------|---|--|
| B3                 | (ignored)   | $\text{RO}_2 \cdot + \text{NO}_2 = \text{NO}_2$  |
|                    |   | This reaction is ignored because of the rapid decomposition of the alkylperoxynitrate back to reactants.   |
| B4                 | FALLOFF<br>4.93E-29 0.0 -4.1<br>5.95E-12 0.0 -3.6<br>0.19 1.0 | $\text{RCO}_3 \cdot + \text{NO}_2 = \text{NO}_2$   |
|                    |   | The rate expression for T=298 K is that recommended by Atkinson (1988) for the reaction of $\text{NO}_2$ with acetyl peroxy radicals. The temperature dependence is assumed to be the same as Atkinson (1988) recommended for $\text{CX}_3\text{O}_2 + \text{NO}_2$ , where X = F or Cl.   |
| B5                 | 1.75E-13 -1.987   | $\text{RO}_2 \cdot + \text{HO}_2 \cdot = \text{HO}_2 \cdot$  |
| B6                 | 1.75E-13 -1.987   | $\text{RCO}_3 \cdot + \text{HO}_2 \cdot = \text{HO}_2 \cdot$   |
|                    |   | Rate constant expression recommended by Atkinson (1988), based on data for the reactions of $\text{HO}_2$ with methyl and ethyl peroxy radicals. The $\text{HO}_2 +$ acetyl peroxy radical reaction is assumed to have the same rate constant.   |
| B8                 | 1.00E-15  | $\text{RO}_2 \cdot + \text{RO}_2 \cdot =$  |
|                    |   | See Carter et al. (1986) for discussion of the choice of this rate constant, which is based on the approximate range of rate constants appropriate for secondary peroxy radicals. As discussed by Atkinson (1988), peroxy + peroxy radical rate constants can vary over orders of magnitude, but separate representation of each of the possible cross-reactions would substantially increase the size and complexity of the mechanism, without significantly affecting its major predictions. Test calculations discussed by Carter et al. (1986) show that use of this approximation does not result in significant differences in results of simulations in propene + n-butane- $\text{NO}_x$ -air mixtures compared with models including separate reactions of all these peroxy + peroxy reactions, with the appropriate rate constants for each. |
| B9                 | 3.00E-12  | $\text{RO}_2 \cdot + \text{RCO}_3 \cdot =$   |
|                    |   | The rate constant used for this reaction is based on the measured value for $\text{CH}_3\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ , as given by Atkinson (1988).   |
| B10                | 5.30E-12  | $\text{RCO}_3 \cdot + \text{RCO}_3 \cdot =$  |

(continued)

Table 2 (continued) - 19

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup> |
|--|---------------------------------|-----------------------|
| The rate constant used for this reaction is the average of the values of Addison et al. (1980) and Basco and Parmar (1985) for the self reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , as tabulated by Atkinson (1988). |                                 |                       |

## REACTIONS OF OTHER PEROXY RADICAL OPERATORS

[The following chemical operators are used to represent net effects of reactions of individual peroxy radicals in the presence or absence of  $\text{NO}_x$ . These are discussed in detail by Lurmann et al. (1987a) and Carter et al. (1987). The kinetics of their reactions are assumed to be the same as used for  $\text{RO}_2$ ., shown above. The steady state approximation can be used for all of these species.]

|     |          |  |
|-----|----------|--|
| B11 | SAMEK B1 | $\text{RO}_2\text{-R.} + \text{NO} = \text{NO}_2 + \text{HO}_2$ .          |
| B12 | SAMEK B5 | $\text{RO}_2\text{-R.} + \text{HO}_2. = -\text{OOH}$                       |
| B13 | SAMEK B8 | $\text{RO}_2\text{-R.} + \text{RO}_2. = \text{RO}_2. + .5 \text{ HO}_2.$   |
| B14 | SAMEK B9 | $\text{RO}_2\text{-R.} + \text{RCO}_3. = \text{RCO}_3. + .5 \text{ HO}_2.$ |

The operator  $\text{RO}_2\text{-R.}$  is used to represent peroxy radical reactions where the net effect in the presence of  $\text{NO}_x$  is the conversion of  $\text{NO}$  to  $\text{NO}_2$  and the generation of  $\text{HO}_2$ . In the absence of  $\text{NO}_x$ , the net effect is either reaction with  $\text{HO}_2$  to form a hydroperoxide group, or reaction with another peroxy radical. By analogy with the self reaction of methyl peroxy radicals (see Atkinson 1988), peroxy + peroxy radical reactions are assumed to react via a radical forming route half the time, with the radical formed being represented by  $\text{HO}_2$ . This operator is a zero carbon radical species.

|     |          |   |
|-----|----------|---|
| B19 | SAMEK B1 | $\text{RO}_2\text{-N.} + \text{NO} = \text{RNO}_3$  |
| B20 | SAMEK B5 | $\text{RO}_2\text{-N.} + \text{HO}_2. = -\text{OOH} + \text{MEK} + .5 \text{ C}$                  |
| B21 | SAMEK B8 | $\text{RO}_2\text{-N.} + \text{RO}_2. = \text{RO}_2. + .5 \text{ HO}_2. + \text{MEK}$<br>+ .5 C   |
| B22 | SAMEK B9 | $\text{RO}_2\text{-N.} + \text{RCO}_3. = \text{RCO}_3. + .5 \text{ HO}_2. + \text{MEK}$<br>+ .5 C |

The operator  $\text{RO}_2\text{-N.}$  is a radical species which is used to represent peroxy radical reactions where the net effect in the presence of  $\text{NO}_x$  is reaction with  $\text{NO}$  to form alkyl nitrates, which are represented by  $\text{RNO}_3$ . In the absence of  $\text{NO}_x$ , the net effect is either reaction with  $\text{HO}_2$  to form a hydroperoxide group, or reaction with another peroxy radical, in a manner analogous to the reactions of  $\text{RO}_2\text{-R.}$ , above, except that this is a five-carbon operator (since  $\text{RNO}_3$  has

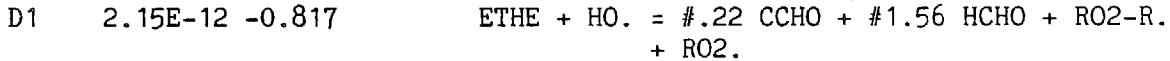
(continued)

Table 2 (continued) - 20

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|--|---------------------------------|--|
| five carbons), and MEK + "lost carbon" is used to represent these carbons when these radicals react in the absence of NO <sub>x</sub> .  |                                 |  |
| G2   | SAMEK B1                        | RO <sub>2</sub> -NP. + NO = NPHE   |
| G3   | SAMEK B5                        | RO <sub>2</sub> -NP. + HO <sub>2</sub> . = -OOH + #6 -C                                      |
| G4   | SAMEK B8                        | RO <sub>2</sub> -NP. + RO <sub>2</sub> . = RO <sub>2</sub> . + #.5 HO <sub>2</sub> . + #6 -C |
| G5   | SAMEK B9                        | RO <sub>2</sub> -NP. + RC <sub>03</sub> . = RC <sub>03</sub> . + HO <sub>2</sub> . + #6 -C   |
| The operator RO <sub>2</sub> -NP. is exactly analogous to RO <sub>2</sub> -N. except that it is used when in aromatic mechanisms where nitrophenols are used to represent the product of the peroxy + NO reaction, rather than the lumped alkyl nitrate RNO <sub>3</sub> . It is a radical species with six carbons. The reactions of the product(s) are formed when the radicals this represents react in the absence of NO <sub>x</sub> are ignored. |                                 |  |
| G2   | SAMEK B1                        | RO <sub>2</sub> -XN. + NO = -N   |
| G3   | SAMEK B5                        | RO <sub>2</sub> -XN. + HO <sub>2</sub> . = -OOH  |
| G4   | SAMEK B8                        | RO <sub>2</sub> -XN. + RO <sub>2</sub> . = RO <sub>2</sub> . + #.5 HO <sub>2</sub> .         |
| G5   | SAMEK B9                        | RO <sub>2</sub> -XN. + RC <sub>03</sub> . = RC <sub>03</sub> . + HO <sub>2</sub> .           |
| The operator RO <sub>2</sub> -XN. is analogous to RO <sub>2</sub> -N. and RO <sub>2</sub> -NP. except that the reactions of the nitrogen-containing product formed when the radicals it represents react with NO are ignored. (It is used primarily to represent the effects of formation of C <sub>3</sub> or smaller organic nitrates, which react only slowly in the atmosphere.). It is a zero carbon radical species.                             |                                 |  |
| B15  | SAMEK B1                        | R <sub>2</sub> O <sub>2</sub> . + NO = NO <sub>2</sub>                                       |
| B16  | SAMEK B5                        | R <sub>2</sub> O <sub>2</sub> . + HO <sub>2</sub> . =  |
| B17  | SAMEK B8                        | R <sub>2</sub> O <sub>2</sub> . + RO <sub>2</sub> . = RO <sub>2</sub> .                      |
| B18  | SAMEK B9                        | R <sub>2</sub> O <sub>2</sub> . + RC <sub>03</sub> . = RC <sub>03</sub> .                    |

The operator R<sub>2</sub>O<sub>2</sub>. is a zero-carbon, non-radical species which is used to represent the net effect of the additional NO to NO<sub>2</sub> conversions resulting from multi-step photooxidation mechanisms involving second- and subsequent-generation peroxy radicals. Its destruction by "reactions" with HO<sub>2</sub> or other peroxy radicals represents the fact that when peroxy radicals react via these routes, the additional NO to NO<sub>2</sub> conversions in multi-step mechanisms do not take place.

## REACTIONS OF ETHENE



(continued)

Table 2 (continued) - 21

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>   |
|---|---------------------------------|---|
| <p>The rate expression is recommended by Atkinson (1986, 1988). Product yields are based on data of Niki et al. (1981). Glycolaldehyde is represented by acetaldehyde.</p>  |                                 |   |
| D6  | 1.20E-14    5.226               | $\text{ETHE} + \text{O}_3 = \text{HCHO} + \# .37 \text{ O3OL-SB} + \# .44 \text{ CO}$ $+ \# .56 \text{ -C} + \# .12 \text{ HO}_2.$  |
| <p>The Rate expression is recommended by Atkinson (1988). The products used are based on assuming the following sets of reactions, which is the mechanism recommended by Atkinson (1988) [which is similar to the mechanism recommended by Atkinson and Lloyd(1984)]:</p> |                                 |   |
|   |                                 | $\text{ETHE} + \text{O}_3 = \text{HCHO} + (\text{HCHO}_2)$ $(\text{HCHO}_2) = \# .37 \text{ O3OL-SB} + \# .44 \text{ CO} + \# .56 \text{ -C} + \# .12 \text{ HO}_2.$  |
|   |                                 | <p>Lost carbon = 0.37 HCOOH + 0.19 CO<sub>2</sub>. The formation of 0.13 H<sub>2</sub> and 0.44 H<sub>2</sub>O is not shown. The operator O3OL-SB is used to represent conversion of SO<sub>2</sub> to SO<sub>3</sub> by ozonolysis intermediates. (See the reactions of SO<sub>2</sub>, above.)</p>  |
| D8  | 1.04E-11    1.574               | $\text{ETHE} + \text{O} = \text{HCHO} + \text{CO} + \text{HO}_2. + \text{R}2\text{O}_2\text{-R}. + \text{R}2\text{O}_2.$  |
|   |                                 | <p>The rate expression and mechanism are based on recommendation of Atkinson and Lloyd (1984). This is the same as used by Carter et al. (1986). The ketene + H<sub>2</sub> pathway is ignored.</p>   |
| D9  | 2.15E-12    5.468               | $\text{ETHE} + \text{NO}_3 = \text{NO}_2 + \# 2 \text{ HCHO} + \text{R}2\text{O}_2. + \text{R}2\text{O}_2.$   |
|   |                                 | <p>The T=298 K rate constant is based on the recommendation of Atkinson (1988). The Arrhenius A factor is assumed to be the same as the OH + ethene reaction.</p>   |
|   |                                 | <p>Note: R<sub>2</sub>O<sub>2</sub>. is used to represent the peroxy radicals formed in this reaction instead of R<sub>2</sub>O<sub>2</sub>-R. because no HO<sub>2</sub> is generated in the NO reaction. However, this results in the formation of -OOH in the HO<sub>2</sub> reaction being neglected, which is an approximation. It also results in no HO<sub>2</sub> being formed in the R<sub>2</sub>O<sub>2</sub>+R<sub>2</sub>O<sub>2</sub> reaction, which is appropriate for this radical.</p> |

#### GENERAL ALKANE AND AROMATIC REACTIONS

The following reaction is included for each lumped or explicitly represented or lumped alkane or aromatic in the mechanism. The species AARn, where n=1, 2, ..., are used to represent reactions

(continued)

Table 2 (continued) - 22

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>   |
|---|---------------------------------|---|
|   |                                 | of one or more alkane or aromatic species, with the values of the OH radical rate constant and the mechanistic parameters varying depending on the individual compound, or group of compounds, being represented. The mechanistic parameters used in this generalized alkane/aromatic reaction are listed and described in Table 4.   |
| AnOH (kAnOH depends on the compound or mixture being represented) |                                 | $\text{HO.} + \text{AARn} = \#AnRR \text{ RO2-R.} + \#AnNR \text{ RO2-N.}$<br>$+ \#AnXN \text{ RO2-XN.} + \#AnNP \text{ RO2-NP.}$<br>$+ \#AnRH \text{ HO2.} + \#AnR2 \text{ R2O2.}$<br>$+ \#AnRO2 \text{ RO2.} + \#AnA1 \text{ HCHO}$<br>$+ \#AnA2 \text{ CCHO} + \#AnA3 \text{ RCHO}$<br>$+ \#AnK3 \text{ ACET} + \#AnK4 \text{ MEK}$<br>$+ \#AnCO \text{ CO} + \#AnC2 \text{ CO2}$<br>$+ \#AnPH \text{ PHEN} + \#AnCR \text{ CRES}$<br>$+ \#AnBZ \text{ BALD} + \#AnGL \text{ GLY}$<br>$+ \#AnMG \text{ MGLY} + \#AnU1 \text{ AFG1}$<br>$+ \#AnU2 \text{ AFG2} + \#AnXC \text{ -C}$ |

Table 6 gives the list of the rate constants and product yield parameters assigned for the alkane species in this mechanism. Footnotes to table 6 indicate how these were derived.

Table 7 gives the list of the rate constants and product yield parameters used for the aromatics which can be represented in the mechanism, and Table 8 gives the parameters for the miscellaneous species (e.g., alcohols, ethers, etc.) which are generally lumped with the alkanes. Comments in those tables give the sources of the rate constant expressions and mechanistic parameter assignments which are used.

Some of the product yield parameters in the above reaction are determined based on the assigned values for the other parameters. These are calculated from the other parameters as indicated in Table 4.

#### GENERAL ALKENE REACTIONS

One set of the following four reactions are included for each lumped alkene in the mechanism. For each alkene or lumped alkene which are represented, the following kinetic and mechanistic parameters must be specified. The mechanistic parameters used in these generalized alkene reactions are listed and described in Table 5. The values of the mechanistic parameters used for the individual alkenes in the mechanism (other than those which are

(continued)

Table 2 (continued) - 23

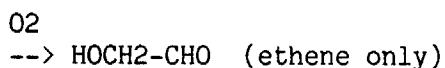
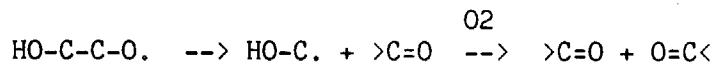
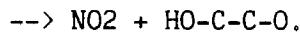
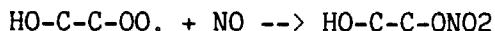
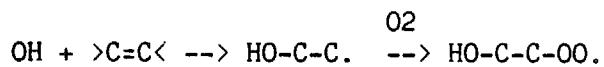
| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup> |
|--------------------|---------------------------------|-----------------------|
|--------------------|---------------------------------|-----------------------|

determined from values of other parameters as shown in Table 5) are given in Table 9.

OnOH (kOnOH depends on the compound or mixture being represented)

OLEn + HO. = #OnP1R HCHO + #OnP2R CCHO  
+ #OnP3R RCHO + #OnP4R ACET  
+ #OnP5R MEK + #OnPR RO2-R.  
+ #OnPN RO2-N. + RO2.  
+ #OnOHXC -C

The parameters for this reaction are derived based on the following generalized OH + alkene reaction mechanism:



Thus, for non-ethene alkenes, the specific product yields thus depend on the substituents about the double bond, and the nitrate yield assumed in the OH reaction. (The parameters in Table 5 also include provision for representing glycolaldehyde formation in this reaction, as would be necessary if this species were representing mixtures containing ethene. However, lumping ethene with other alkenes is not recommended.)

OnO3 (kOnO3 depends on the compound or mixture being represented)

OLEn + O3 = #OnO3A1 HCHO + #OnO3A2 CCHO  
+ #OnO3A3 RCHO + #OnO3K3 ACET  
+ #OnO3K4 MEK + #OnO3MG MGLY  
+ #OnO3CO CO + #OnO3SB O3OL-SB  
+ #OnO3P1 CCO-02.  
+ #OnO3P2 C2CO-02. #OnO3RH HO2.  
+ #OnO3OH HO. + #OnO3RR RO2-R.  
+ #OnO3R2 R2O2. + #OnO3R02 RO2.  
+ #OnO3PS RC03. + #OnO3XC -C

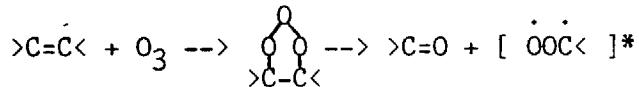
The product yield parameters are calculated from the structural parameters input as shown in Table 5. They are based on the following generalized ozone - alkene reaction mechanism:

(continued)

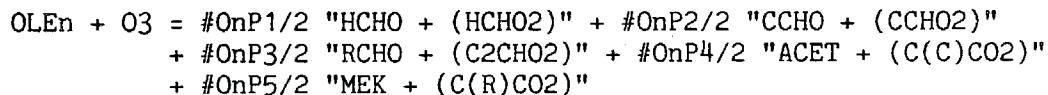
Table 2 (continued) - 24

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup> |
|--------------------|---------------------------------|-----------------------|
|--------------------|---------------------------------|-----------------------|

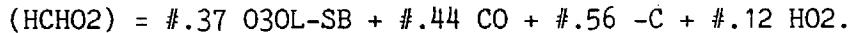
The initial reaction is assumed to be of the type



where the species  $[\text{OO'C}]^*$  is an initially formed excited Criegee intermediate, which reacts further, depending on its substituents, as indicated below. In terms of the parameters and species in this mechanism, this initial reaction can be represented as follows, where the species in parentheses represent the excited biradicals, which are represented in the overall reaction by the sets of products which they are assumed to ultimately form.



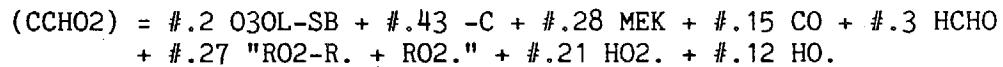
The species  $(\text{HCHO}_2)$  represents the initially formed excited Criegee intermediate formed in the reactions of ozone with alkenes with  $=\text{CH}_2$  groups. The mechanism assumed for it, which is based on data for ethene, is as follows:



This mechanism is recommended by Atkinson (1988). It is similar to that recommended by Atkinson and Lloyd (1984). The lost carbon shown above represents  $0.37 \text{ HCOOH} + 0.19 \text{ CO}_2$ . The mechanism also predicts the formation of  $0.13 \text{ H}_2$  and  $0.44 \text{ H}_2\text{O}$ , which are not shown.

The operator  $\text{O3OL-SB}$  is used to represent conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the stabilized ozonolysis intermediates. Its reactions are given above in conjunction with the  $\text{SO}_2$  reactions.

The species  $(\text{CCHO}_2)$  represents the excited intermediate initially formed in the reactions of ozone with alkenes with  $=\text{CH}(\text{CH}_3)$  groups. Its mechanism, based on data for propene and 2-butenes, is as follows:



This mechanism is based on the stabilization yields of Hatakeyama et al. (1984) and the fragmentation mechanism recommended by

(continued)

Table 2 (continued) - 25

| Label <sup>a</sup>   | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup> |
|--|---------------------------------|-----------------------|
| Atkinson and Lloyd (1984). The total fragmentation yield was reduced in order to fit chamber data, as discussed by Carter et al. (1986). This is the same mechanism as used by Carter et al. (1984), except that MEK is used to represent the unaccounted-for carbon in this reaction. The lost carbon represents 0.14 CH <sub>4</sub> + 0.29 CO <sub>2</sub> .  |                                 |                       |
| The species (C <sub>2</sub> CHO <sub>2</sub> ) represents the excited intermediate initially formed in the reactions of ozone with alkenes with =CH(R) groups, where R is not H or methyl. Its reactions are assumed to be as follows:   |                                 |                       |
| (C <sub>2</sub> CHO <sub>2</sub> ) = #.2 O <sub>3</sub> OL-SB + #.57 -C + #.42 MEK + #.15 CO + #.3 CCHO + #.27 "R02-R. + R02." + #.21 HO2. + #.12 HO.  |                                 |                       |
| This is the same as the mechanism assumed by Carter et al. (1986) in the detailed mechanism for 1-butene, except that the carbon in the uncharacterized products is represented by MEK. The "lost carbon" represents 0.14 C <sub>2</sub> + 0.29 CO <sub>2</sub> .  |                                 |                       |
| The species (C(C)CO <sub>2</sub> ) represents the excited intermediate initially formed in the reactions of ozone with alkenes containing =C(CH <sub>3</sub> ) <sub>2</sub> groups. The reactions assumed for this are as follows:   |                                 |                       |
| (C(C)CO <sub>2</sub> ) = #.2 "HO. + CCOCHO + R02-R. + R02." + #.8 MEK + #-.8 -C  |                                 |                       |
| The mechanism assumed by Carter et al. (1986) in the detailed mechanism for isobutene is employed. This assumes 20% decomposition and 80% stabilization, based roughly on fits to a single chamber run, with the stabilization product being represented by MEK. The biradical is assumed to rapidly re-arrange prior to stabilization or decomposition, so it does not react with SO <sub>2</sub> . Therefore, O <sub>3</sub> OL-SB is not a product. |                                 |                       |
| The species (C(R)CO <sub>2</sub> ) represents the excited intermediates initially formed in the reactions of ozone with alkenes containing =C(CH <sub>3</sub> )(R) groups. The mechanism assumed for this species is as follows:   |                                 |                       |
| (C(R)CO <sub>2</sub> ) = #.2 "HO. + RC03." + #.1 "CCHO + HCHO + CCO-O2. + C2CO-O2." + #.3 "R2O2. + R02." + #.8 MEK   |                                 |                       |

(continued)

Table 2 (continued) - 26

| Label <sup>a</sup>  | Kinetic Parameters <sup>b</sup>                              | Reaction <sup>c</sup>  |
|---|--|--|
| This mechanism is estimated by analogy to the mechanism used by Carter et al. (1986) for (C(C)CO <sub>2</sub> ). In this case, OH + C-C(.)-CO-C is formed 20% of the time, instead of OH + .C-CO-C in the case of (C(C)CO <sub>2</sub> ). In both cases, the stabilization product (formed 80% of the time) is represented by MEK. No reaction with SO <sub>2</sub> is assumed.   |  |  |
| Based on the above mechanisms, the product yields used for the overall ozone - alkene reactions are calculated as shown in Table 5.   |  |  |
| OnOA  | (kOnOA depends on the compound or mixture being represented) | OLEn + O = #.4 HO <sub>2</sub> . + #.5 "MEK + RCHO" + #OnOAXC -C   |
| The lumped model for this reaction cannot be made to be equivalent to the detailed models by using appropriate values of the structural parameters. The reactions used in the detailed model of Carter et al. (1986) are listed below. The above generalized mechanism is approximation of these. It is not valid for ethene.   |  |  |
| $\text{Propene} + \text{O} = \# .6 \text{ RCHO} + \# .4 \text{ CO} + \# .4 \text{ C-O}_2. + \# .2 \text{ C}_2\text{-O}_2.$<br>$\quad \quad \quad + \# .2 \text{ HO}_2. + \# .6 \text{ RO}_2.$<br>$\text{1-Butene} + \text{O} = \# .44 \text{ MEK} + \# .39 \text{ "RCHO} + \text{-C"} + \# .17 \text{ "CO} + \text{HCHO}$<br>$\quad \quad \quad + \text{CCHO"} + \# .34 \text{ HO}_2.$<br>$\text{2-Butenes} + \text{O} = \text{MEK} + \# .4 \text{ HO}_2.$<br>$\text{Isobutene} + \text{O} = \# .5 \text{ "MEK} + \text{RCHO} + \text{-C"} + \# .4 \text{ HO}_2.$ |  |  |
| The carbon lost from this reaction is calculated from the number of carbons in the alkene as shown in Table 5.  |  |  |
| OnN3  | (kOnN3 depends on the compound or mixture being represented) | OLEn + NO <sub>3</sub> = NO <sub>2</sub> + #OnP1 HCHO + #OnP2 CCHO + #OnP3 RCHO + #OnP4 ACET + #OnP5 MEK + R2O <sub>2</sub> . + RO <sub>2</sub> . + #OnN3XC -C |
| The general mechanism for this reaction is the same as that used by Carter et al. (1986), and is as follows:  |  |  |
| $\text{>C=C<} + \text{NO}_3 \rightarrow \text{O}_2\text{NO-C-C.} \xrightarrow{\text{O}_2} \text{O}_2\text{NO-C-C-OO.}$<br>$\text{O}_2\text{NO-C-C-OO.} + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2\text{NO-C-C-O.}$<br>$\text{O}_2\text{NOC-C-O.} \xrightarrow{\text{fast}} \text{NO}_2 + \text{>C=O} + \text{O=C<}$   |  |  |
| (continued)   |  |  |

Table 2 (continued) - 27

| Label <sup>a</sup> | Kinetic Parameters <sup>b</sup> | Reaction <sup>c</sup>  |
|--------------------|---------------------------------|--|
|                    |                                 | This is analogous to the OH mechanism, except that there is no nitrate or glycolaldehyde formation, and the intermediate radical is assumed to form NO <sub>2</sub> when it decomposes. R <sub>2</sub> O <sub>2</sub> . is used to represent the peroxy radicals formed in this reaction instead of RO <sub>2</sub> -R. because no HO <sub>2</sub> is generated in the NO reaction. However, this results in the formation of -OOH in the HO <sub>2</sub> reaction to be neglected, which is an approximation. It also results in no HO <sub>2</sub> being formed in the RO <sub>2</sub> +RO <sub>2</sub> reaction, which is appropriate for this radical. |

The amount of carbon lost in this reaction is calculated from the number of carbons in the alkene and the structural parameters as indicated in Table 5.

<sup>a</sup>Reaction label notation of Carter et al. (1986) is employed for all reactions in this mechanism, except for new reactions which have been added.

<sup>b</sup>The kinetic parameters in the mechanism are specified in one of four ways:

1. Simple thermal reactions:

If the kinetic parameters are given as one to three numbers without any additional notation, then the numbers given are (in order) A, Ea, and B, and the rate constant, k, is calculated by the modified Arrhenius expression.

$$k = A \times (T/300)^B \times \exp [-Ea / (0.0019872 \times T)]$$

where T is the temperature in K, Ea is given in kcal mole<sup>-1</sup>, and the units of k and A are in cm - molecule - second units. If only one number is given, then Ea and B are zero, i.e., there is no temperature dependence. If two numbers are given, then B = 0.

2. "Falloff" thermal reactions:

If the kinetic parameters are given as seven numbers in the following format,

|                |                 |                |
|----------------|-----------------|----------------|
| FALLOFF        |                 |                |
| A <sub>0</sub> | Ea <sub>0</sub> | B <sub>0</sub> |
| A <sub>∞</sub> | Ea <sub>∞</sub> | B <sub>∞</sub> |
| F              | n               |                |

(continued)

Table 2 (continued) - 28

then the rate constant,  $k$ , is calculated by

$$k = [(k_0 \times M) / (1 + [k_0 \times M / k_\infty])] \times f^g$$

where

$$g = 1/[1 + (\log_{10} [k_0 \times M / k_\infty] / n)^2]$$

and

$$\begin{aligned} k_0 &= A_0 \times (T/300)^{B_0} \times \exp(-Ea_0 / [0.0019872 \times T]) \\ k_\infty &= A_\infty \times (T/300)^{B_\infty} \times \exp(-Ea_\infty / [0.0019872 \times T]) \end{aligned}$$

and  $T$  is the temperature in K and  $M$  is the concentration of the constant species "M," which is the total pressure in molecules  $\text{cm}^{-3}$ .

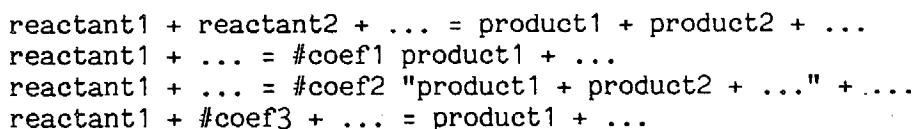
### 3. Reactions with same rate constants as other reactions:

The notation "SAMEK xxxx", where "xxxx" is the reaction label for some other reaction, means that the reaction always has the same rate constant as reaction "xxxx".

### 4. Photolysis reactions:

Photolysis reactions are indicated by the notation "PHOT=filename," where "filename" refers to a "photolysis file," which gives the absorption coefficients and quantum yields, as a function of wavelength, which are used to calculate the photolysis rate constants given the spectral distribution of the light source. The contents of the photolysis files used in this mechanism are given in Table 3.

<sup>c</sup>The following examples indicate the notation used to define the reactants, products, and (where applicable) coefficients involved in the reactions in the mechanism:



The first example is a simple reaction without any product yield coefficients, i.e., all products shown have unit yields. The second and third have product coefficients which give the yield of the products. The notation in the third reaction is used to indicate that both "product1" and "product2" have the same coefficient, and thus that reaction is equivalent to

(continued)

Table 2 (continued) - 29

reactant1 + ... = #coef1 product1 + #coef2 product2 + ...

When a coefficient is shown as a "reactant", as in the fourth example, the coefficient is multiplied by the rate constant calculated from the kinetic parameters (as described in footnote b, above), to give the rate constant of the reaction.

A special kind of reactant coefficient is that of the form "#RCONxxxx," whose value is the rate constant for the reaction labeled "xxxx." Usually, the reaction labeled "xxxx" is the reverse of this reaction, and the "kinetic parameters" given actually refer to an equilibrium constant.

Table 3... Tabulation of Absorption Coefficients (ABS) and Quantum Yields (QY) Used for All Photolysis Reactions in the Detailed Mechanism

| PHOT<br>Name       | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------------|------------|----------------------------|-------|------------|----------------------------|-------|
| NO2                | 250.0      | 2.83E-20                   | 1.000 | 255.0      | 1.45E-20                   | 1.000 |
|                    | 260.0      | 1.90E-20                   | 1.000 | 265.0      | 2.05E-20                   | 1.000 |
|                    | 270.0      | 3.13E-20                   | 1.000 | 275.0      | 4.02E-20                   | 1.000 |
|                    | 280.0      | 5.54E-20                   | 1.000 | 285.0      | 6.99E-20                   | 1.000 |
|                    | 290.0      | 8.18E-20                   | 0.999 | 295.0      | 9.67E-20                   | 0.998 |
|                    | 300.0      | 1.17E-19                   | 0.997 | 305.0      | 1.66E-19                   | 0.996 |
|                    | 310.0      | 1.76E-19                   | 0.995 | 315.0      | 2.25E-19                   | 0.994 |
|                    | 320.0      | 2.54E-19                   | 0.993 | 325.0      | 2.79E-19                   | 0.992 |
|                    | 330.0      | 2.99E-19                   | 0.991 | 335.0      | 3.45E-19                   | 0.990 |
|                    | 340.0      | 3.88E-19                   | 0.989 | 345.0      | 4.07E-19                   | 0.988 |
|                    | 350.0      | 4.10E-19                   | 0.987 | 355.0      | 5.13E-19                   | 0.986 |
|                    | 360.0      | 4.51E-19                   | 0.984 | 365.0      | 5.78E-19                   | 0.983 |
|                    | 370.0      | 5.42E-19                   | 0.981 | 375.0      | 5.35E-19                   | 0.979 |
|                    | 380.0      | 5.99E-19                   | 0.975 | 381.0      | 5.98E-19                   | 0.974 |
|                    | 382.0      | 5.97E-19                   | 0.973 | 383.0      | 5.96E-19                   | 0.972 |
|                    | 384.0      | 5.95E-19                   | 0.971 | 385.0      | 5.94E-19                   | 0.969 |
|                    | 386.0      | 5.95E-19                   | 0.967 | 387.0      | 5.96E-19                   | 0.966 |
|                    | 388.0      | 5.98E-19                   | 0.964 | 389.0      | 5.99E-19                   | 0.962 |
|                    | 390.0      | 6.00E-19                   | 0.960 | 391.0      | 5.98E-19                   | 0.959 |
|                    | 392.0      | 5.96E-19                   | 0.957 | 393.0      | 5.93E-19                   | 0.953 |
|                    | 394.0      | 5.91E-19                   | 0.950 | 395.0      | 5.89E-19                   | 0.942 |
|                    | 396.0      | 6.06E-19                   | 0.922 | 397.0      | 6.24E-19                   | 0.870 |
|                    | 398.0      | 6.41E-19                   | 0.820 | 399.0      | 6.59E-19                   | 0.760 |
|                    | 400.0      | 6.76E-19                   | 0.695 | 401.0      | 6.67E-19                   | 0.635 |
|                    | 402.0      | 6.58E-19                   | 0.560 | 403.0      | 6.50E-19                   | 0.485 |
|                    | 404.0      | 6.41E-19                   | 0.425 | 405.0      | 6.32E-19                   | 0.350 |
|                    | 406.0      | 6.21E-19                   | 0.290 | 407.0      | 6.10E-19                   | 0.225 |
|                    | 408.0      | 5.99E-19                   | 0.185 | 409.0      | 5.88E-19                   | 0.153 |
|                    | 410.0      | 5.77E-19                   | 0.130 | 411.0      | 5.88E-19                   | 0.110 |
|                    | 412.0      | 5.98E-19                   | 0.094 | 413.0      | 6.09E-19                   | 0.083 |
|                    | 414.0      | 6.19E-19                   | 0.070 | 415.0      | 6.30E-19                   | 0.059 |
|                    | 416.0      | 6.29E-19                   | 0.048 | 417.0      | 6.27E-19                   | 0.039 |
|                    | 418.0      | 6.26E-19                   | 0.030 | 419.0      | 6.24E-19                   | 0.023 |
|                    | 420.0      | 6.23E-19                   | 0.018 | 421.0      | 6.18E-19                   | 0.012 |
|                    | 422.0      | 6.14E-19                   | 0.008 | 423.0      | 6.09E-19                   | 0.004 |
|                    | 424.0      | 6.05E-19                   | 0.000 | 425.0      | 6.00E-19                   | 0.000 |
| NO <sub>3</sub> NO | 585.0      | 2.77E-18                   | 0.000 | 590.0      | 5.14E-18                   | 0.250 |
|                    | 595.0      | 4.08E-18                   | 0.400 | 600.0      | 2.83E-18                   | 0.250 |
|                    | 605.0      | 3.45E-18                   | 0.200 | 610.0      | 1.48E-18                   | 0.200 |
|                    | 615.0      | 1.96E-18                   | 0.100 | 620.0      | 3.58E-18                   | 0.100 |
|                    | 625.0      | 9.25E-18                   | 0.050 | 630.0      | 5.66E-18                   | 0.050 |
|                    | 635.0      | 1.45E-18                   | 0.030 | 640.0      | 1.11E-18                   | 0.000 |

(continued)

Table 3 (continued) - 2

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
| N03N02       | 400.0      | 0.00E-01                   | 1.000 | 405.0      | 3.00E-20                   | 1.000 |
|              | 410.0      | 4.00E-20                   | 1.000 | 415.0      | 5.00E-20                   | 1.000 |
|              | 420.0      | 8.00E-20                   | 1.000 | 425.0      | 1.00E-19                   | 1.000 |
|              | 430.0      | 1.30E-19                   | 1.000 | 435.0      | 1.80E-19                   | 1.000 |
|              | 440.0      | 1.90E-19                   | 1.000 | 445.0      | 2.20E-19                   | 1.000 |
|              | 450.0      | 2.80E-19                   | 1.000 | 455.0      | 3.30E-19                   | 1.000 |
|              | 460.0      | 3.70E-19                   | 1.000 | 465.0      | 4.30E-19                   | 1.000 |
|              | 470.0      | 5.10E-19                   | 1.000 | 475.0      | 6.00E-19                   | 1.000 |
|              | 480.0      | 6.40E-19                   | 1.000 | 485.0      | 6.90E-19                   | 1.000 |
|              | 490.0      | 8.80E-19                   | 1.000 | 495.0      | 9.50E-19                   | 1.000 |
|              | 500.0      | 1.01E-18                   | 1.000 | 505.0      | 1.10E-18                   | 1.000 |
|              | 510.0      | 1.32E-18                   | 1.000 | 515.0      | 1.40E-18                   | 1.000 |
|              | 520.0      | 1.45E-18                   | 1.000 | 525.0      | 1.48E-18                   | 1.000 |
|              | 530.0      | 1.94E-18                   | 1.000 | 535.0      | 2.04E-18                   | 1.000 |
|              | 540.0      | 1.81E-18                   | 1.000 | 545.0      | 1.81E-18                   | 1.000 |
|              | 550.0      | 2.36E-18                   | 1.000 | 555.0      | 2.68E-18                   | 1.000 |
|              | 560.0      | 3.07E-18                   | 1.000 | 565.0      | 2.53E-18                   | 1.000 |
|              | 570.0      | 2.54E-18                   | 1.000 | 575.0      | 2.74E-18                   | 1.000 |
|              | 580.0      | 3.05E-18                   | 1.000 | 585.0      | 2.77E-18                   | 1.000 |
|              | 590.0      | 5.14E-18                   | 0.750 | 595.0      | 4.08E-18                   | 0.600 |
|              | 600.0      | 2.83E-18                   | 0.550 | 605.0      | 3.45E-18                   | 0.400 |
|              | 610.0      | 1.45E-18                   | 0.300 | 615.0      | 1.96E-18                   | 0.250 |
|              | 620.0      | 3.58E-18                   | 0.200 | 625.0      | 9.25E-18                   | 0.150 |
|              | 630.0      | 5.66E-18                   | 0.050 | 635.0      | 1.45E-18                   | 0.000 |
| 0303P        | 280.0      | 3.97E-18                   | 0.100 | 281.0      | 3.60E-18                   | 0.100 |
|              | 282.0      | 3.24E-18                   | 0.100 | 283.0      | 3.01E-18                   | 0.100 |
|              | 284.0      | 2.73E-18                   | 0.100 | 285.0      | 2.44E-18                   | 0.100 |
|              | 286.0      | 2.21E-18                   | 0.100 | 287.0      | 2.01E-18                   | 0.100 |
|              | 288.0      | 1.76E-18                   | 0.100 | 289.0      | 1.58E-18                   | 0.100 |
|              | 290.0      | 1.41E-18                   | 0.100 | 291.0      | 1.26E-18                   | 0.100 |
|              | 292.0      | 1.10E-18                   | 0.100 | 293.0      | 9.89E-19                   | 0.100 |
|              | 294.0      | 8.59E-19                   | 0.100 | 295.0      | 7.70E-19                   | 0.100 |
|              | 296.0      | 6.67E-19                   | 0.100 | 297.0      | 5.84E-19                   | 0.100 |
|              | 298.0      | 5.07E-19                   | 0.100 | 299.0      | 4.52E-19                   | 0.100 |
|              | 300.0      | 3.92E-19                   | 0.100 | 301.0      | 3.42E-19                   | 0.100 |
|              | 302.0      | 3.06E-19                   | 0.100 | 303.0      | 2.60E-19                   | 0.100 |
|              | 304.0      | 2.37E-19                   | 0.100 | 305.0      | 2.01E-19                   | 0.112 |
|              | 306.0      | 1.79E-19                   | 0.149 | 307.0      | 1.56E-19                   | 0.197 |
|              | 308.0      | 1.38E-19                   | 0.259 | 309.0      | 1.25E-19                   | 0.339 |
|              | 310.0      | 1.02E-19                   | 0.437 | 311.0      | 9.17E-20                   | 0.546 |
|              | 312.0      | 7.88E-20                   | 0.652 | 313.0      | 6.77E-20                   | 0.743 |
|              | 314.0      | 6.35E-20                   | 0.816 | 315.0      | 5.10E-20                   | 0.872 |
|              | 316.0      | 4.61E-20                   | 0.916 | 317.0      | 4.17E-20                   | 0.949 |
|              | 318.0      | 3.72E-20                   | 0.976 | 319.0      | 2.69E-20                   | 0.997 |

(continued)

Table 3 (continued) - 3

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
|              | 320.0      | 3.23E-20                   | 1.000 | 330.0      | 6.70E-21                   | 1.000 |
|              | 340.0      | 1.70E-21                   | 1.000 | 350.0      | 4.00E-22                   | 1.000 |
|              | 355.0      | 0.00E-01                   | 1.000 | 400.0      | 0.00E-01                   | 1.000 |
|              | 450.0      | 1.60E-22                   | 1.000 | 500.0      | 1.34E-21                   | 1.000 |
|              | 550.0      | 3.32E-21                   | 1.000 | 600.0      | 5.06E-21                   | 1.000 |
|              | 650.0      | 2.45E-21                   | 1.000 | 700.0      | 8.70E-22                   | 1.000 |
|              | 750.0      | 3.20E-22                   | 1.000 | 800.0      | 1.60E-22                   | 1.000 |
|              | 900.0      | 0.00E-01                   | 1.000 |            |                            |       |
| 0301D        | 280.0      | 3.97E-18                   | 0.900 | 281.0      | 3.60E-18                   | 0.900 |
|              | 282.0      | 3.24E-18                   | 0.900 | 283.0      | 3.01E-18                   | 0.900 |
|              | 284.0      | 2.73E-18                   | 0.900 | 285.0      | 2.44E-18                   | 0.900 |
|              | 286.0      | 2.21E-18                   | 0.900 | 287.0      | 2.01E-18                   | 0.900 |
|              | 288.0      | 1.76E-18                   | 0.900 | 289.0      | 1.58E-18                   | 0.900 |
|              | 290.0      | 1.41E-18                   | 0.900 | 291.0      | 1.26E-18                   | 0.900 |
|              | 292.0      | 1.10E-18                   | 0.900 | 293.0      | 9.89E-19                   | 0.900 |
|              | 294.0      | 8.59E-19                   | 0.900 | 295.0      | 7.70E-19                   | 0.900 |
|              | 296.0      | 6.67E-19                   | 0.900 | 297.0      | 5.84E-19                   | 0.900 |
|              | 298.0      | 5.07E-19                   | 0.900 | 299.0      | 4.52E-19                   | 0.900 |
|              | 300.0      | 3.92E-19                   | 0.900 | 301.0      | 3.42E-19                   | 0.900 |
|              | 302.0      | 3.06E-19                   | 0.900 | 303.0      | 2.60E-19                   | 0.900 |
|              | 304.0      | 2.37E-19                   | 0.900 | 305.0      | 2.01E-19                   | 0.888 |
|              | 306.0      | 1.79E-19                   | 0.851 | 307.0      | 1.56E-19                   | 0.803 |
|              | 308.0      | 1.38E-19                   | 0.741 | 309.0      | 1.25E-19                   | 0.661 |
|              | 310.0      | 1.02E-19                   | 0.563 | 311.0      | 9.17E-20                   | 0.454 |
|              | 312.0      | 7.88E-20                   | 0.348 | 313.0      | 6.77E-20                   | 0.257 |
|              | 314.0      | 6.35E-20                   | 0.184 | 315.0      | 5.10E-20                   | 0.128 |
|              | 316.0      | 4.61E-20                   | 0.084 | 317.0      | 4.17E-20                   | 0.051 |
|              | 318.0      | 3.72E-20                   | 0.024 | 319.0      | 2.69E-20                   | 0.003 |
|              | 320.0      | 3.23E-20                   | 0.000 |            |                            |       |
| HONO         | 311.0      | 0.00E-01                   | 1.000 | 312.0      | 2.00E-21                   | 1.000 |
|              | 313.0      | 4.20E-21                   | 1.000 | 314.0      | 4.60E-21                   | 1.000 |
|              | 315.0      | 4.20E-21                   | 1.000 | 316.0      | 3.00E-21                   | 1.000 |
|              | 317.0      | 4.60E-21                   | 1.000 | 318.0      | 3.60E-20                   | 1.000 |
|              | 319.0      | 6.10E-20                   | 1.000 | 320.0      | 2.10E-20                   | 1.000 |
|              | 321.0      | 4.27E-20                   | 1.000 | 322.0      | 4.01E-20                   | 1.000 |
|              | 323.0      | 3.93E-20                   | 1.000 | 324.0      | 4.01E-20                   | 1.000 |
|              | 325.0      | 4.04E-20                   | 1.000 | 326.0      | 3.13E-20                   | 1.000 |
|              | 327.0      | 4.12E-20                   | 1.000 | 328.0      | 7.55E-20                   | 1.000 |
|              | 329.0      | 6.64E-20                   | 1.000 | 330.0      | 7.29E-20                   | 1.000 |
|              | 331.0      | 8.70E-20                   | 1.000 | 332.0      | 1.38E-19                   | 1.000 |
|              | 333.0      | 5.91E-20                   | 1.000 | 334.0      | 5.91E-20                   | 1.000 |
|              | 335.0      | 6.45E-20                   | 1.000 | 336.0      | 5.91E-20                   | 1.000 |
|              | 337.0      | 4.58E-20                   | 1.000 | 338.0      | 1.91E-19                   | 1.000 |

(continued)

Table 3 (continued) - 4

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
|              | 339.0      | 1.63E-19                   | 1.000 | 340.0      | 1.05E-19                   | 1.000 |
|              | 341.0      | 8.70E-20                   | 1.000 | 342.0      | 3.35E-19                   | 1.000 |
|              | 343.0      | 2.01E-19                   | 1.000 | 344.0      | 1.02E-19                   | 1.000 |
|              | 345.0      | 8.54E-20                   | 1.000 | 346.0      | 8.32E-20                   | 1.000 |
|              | 347.0      | 8.20E-20                   | 1.000 | 348.0      | 7.49E-20                   | 1.000 |
|              | 349.0      | 7.13E-20                   | 1.000 | 350.0      | 6.83E-20                   | 1.000 |
|              | 351.0      | 1.74E-19                   | 1.000 | 352.0      | 1.14E-19                   | 1.000 |
|              | 353.0      | 3.71E-19                   | 1.000 | 354.0      | 4.96E-19                   | 1.000 |
|              | 355.0      | 2.46E-19                   | 1.000 | 356.0      | 1.19E-19                   | 1.000 |
|              | 357.0      | 9.35E-20                   | 1.000 | 358.0      | 7.78E-20                   | 1.000 |
|              | 359.0      | 7.29E-20                   | 1.000 | 360.0      | 6.83E-20                   | 1.000 |
|              | 361.0      | 6.90E-20                   | 1.000 | 362.0      | 7.32E-20                   | 1.000 |
|              | 363.0      | 9.00E-20                   | 1.000 | 364.0      | 1.21E-19                   | 1.000 |
|              | 365.0      | 1.33E-19                   | 1.000 | 366.0      | 2.13E-19                   | 1.000 |
|              | 367.0      | 3.52E-19                   | 1.000 | 368.0      | 4.50E-19                   | 1.000 |
|              | 369.0      | 2.93E-19                   | 1.000 | 370.0      | 1.19E-19                   | 1.000 |
|              | 371.0      | 9.46E-20                   | 1.000 | 372.0      | 8.85E-20                   | 1.000 |
|              | 373.0      | 7.44E-20                   | 1.000 | 374.0      | 4.77E-20                   | 1.000 |
|              | 375.0      | 2.70E-20                   | 1.000 | 376.0      | 1.90E-20                   | 1.000 |
|              | 377.0      | 1.50E-20                   | 1.000 | 378.0      | 1.90E-20                   | 1.000 |
|              | 379.0      | 5.80E-20                   | 1.000 | 380.0      | 7.78E-20                   | 1.000 |
|              | 381.0      | 1.14E-19                   | 1.000 | 382.0      | 1.40E-19                   | 1.000 |
|              | 383.0      | 1.72E-19                   | 1.000 | 384.0      | 1.99E-19                   | 1.000 |
|              | 385.0      | 1.90E-19                   | 1.000 | 386.0      | 1.19E-19                   | 1.000 |
|              | 387.0      | 5.65E-20                   | 1.000 | 388.0      | 3.20E-20                   | 1.000 |
|              | 389.0      | 1.90E-20                   | 1.000 | 390.0      | 1.20E-20                   | 1.000 |
|              | 391.0      | 5.00E-21                   | 1.000 | 392.0      | 0.00E-01                   | 1.000 |
| H2O2         | 250.0      | 8.30E-20                   | 1.000 | 255.0      | 6.70E-20                   | 1.000 |
|              | 260.0      | 5.20E-20                   | 1.000 | 265.0      | 4.20E-20                   | 1.000 |
|              | 270.0      | 3.20E-20                   | 1.000 | 275.0      | 2.50E-20                   | 1.000 |
|              | 280.0      | 2.00E-20                   | 1.000 | 285.0      | 1.50E-20                   | 1.000 |
|              | 290.0      | 1.13E-20                   | 1.000 | 295.0      | 8.70E-21                   | 1.000 |
|              | 300.0      | 6.60E-21                   | 1.000 | 305.0      | 4.90E-21                   | 1.000 |
|              | 310.0      | 3.70E-21                   | 1.000 | 315.0      | 2.80E-21                   | 1.000 |
|              | 320.0      | 2.00E-21                   | 1.000 | 325.0      | 1.50E-21                   | 1.000 |
|              | 330.0      | 1.20E-21                   | 1.000 | 335.0      | 9.00E-22                   | 1.000 |
|              | 340.0      | 7.00E-22                   | 1.000 | 345.0      | 5.00E-22                   | 1.000 |
|              | 350.0      | 3.00E-22                   | 1.000 | 355.0      | 0.00E-01                   | 1.000 |
| HCHOAVGR     | 281.0      | 1.62E-20                   | 0.602 | 282.0      | 9.77E-21                   | 0.614 |
|              | 283.0      | 5.96E-21                   | 0.626 | 284.0      | 3.31E-20                   | 0.638 |
|              | 285.0      | 4.09E-20                   | 0.650 | 286.0      | 2.42E-20                   | 0.662 |
|              | 287.0      | 1.22E-20                   | 0.674 | 288.0      | 2.19E-20                   | 0.686 |
|              | 289.0      | 3.14E-20                   | 0.698 | 290.0      | 1.54E-20                   | 0.710 |

(continued)

Table 3 (continued) - 5

| PHOT<br>Name | WL<br>(nm) | Abs <sub>X</sub><br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs <sub>X</sub><br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|---|-------|------------|---|-------|
|              | 291.0      | 1.49E-20                                | 0.717 | 292.0      | 9.59E-21                                | 0.724 |
|              | 293.0      | 3.22E-20                                | 0.731 | 294.0      | 5.45E-20                                | 0.738 |
|              | 295.0      | 4.07E-20                                | 0.745 | 296.0      | 2.41E-20                                | 0.752 |
|              | 297.0      | 1.79E-20                                | 0.759 | 298.0      | 3.16E-20                                | 0.766 |
|              | 299.0      | 2.81E-20                                | 0.773 | 300.0      | 1.14E-20                                | 0.780 |
|              | 301.0      | 1.27E-20                                | 0.779 | 302.0      | 1.21E-20                                | 0.778 |
|              | 303.0      | 2.78E-20                                | 0.777 | 304.0      | 5.40E-20                                | 0.776 |
|              | 305.0      | 5.30E-20                                | 0.775 | 306.0      | 4.13E-20                                | 0.774 |
|              | 307.0      | 2.23E-20                                | 0.773 | 308.0      | 1.77E-20                                | 0.772 |
|              | 309.0      | 2.43E-20                                | 0.771 | 310.0      | 2.00E-20                                | 0.770 |
|              | 311.0      | 9.15E-21                                | 0.755 | 312.0      | 1.05E-20                                | 0.740 |
|              | 313.0      | 1.43E-20                                | 0.725 | 314.0      | 3.07E-20                                | 0.710 |
|              | 315.0      | 4.50E-20                                | 0.695 | 316.0      | 3.29E-20                                | 0.680 |
|              | 317.0      | 3.77E-20                                | 0.665 | 318.0      | 3.10E-20                                | 0.650 |
|              | 319.0      | 1.22E-20                                | 0.635 | 320.0      | 1.26E-20                                | 0.620 |
|              | 321.0      | 1.48E-20                                | 0.589 | 322.0      | 7.70E-21                                | 0.558 |
|              | 323.0      | 4.66E-21                                | 0.527 | 324.0      | 7.11E-21                                | 0.496 |
|              | 325.0      | 1.51E-20                                | 0.465 | 326.0      | 3.90E-20                                | 0.434 |
|              | 327.0      | 3.50E-20                                | 0.403 | 328.0      | 1.49E-20                                | 0.372 |
|              | 329.0      | 2.30E-20                                | 0.341 | 330.0      | 3.05E-20                                | 0.310 |
|              | 331.0      | 1.43E-20                                | 0.279 | 332.0      | 4.22E-21                                | 0.248 |
|              | 333.0      | 2.01E-21                                | 0.217 | 334.0      | 1.66E-21                                | 0.186 |
|              | 335.0      | 9.68E-22                                | 0.155 | 336.0      | 1.57E-21                                | 0.124 |
|              | 337.0      | 3.27E-21                                | 0.093 | 338.0      | 1.38E-20                                | 0.062 |
|              | 339.0      | 3.18E-20                                | 0.031 | 340.0      | 2.39E-20                                | 0.000 |
| HCHOAVGM     | 281.0      | 1.62E-20                                | 0.341 | 282.0      | 9.77E-21                                | 0.332 |
|              | 283.0      | 5.96E-21                                | 0.323 | 284.0      | 3.31E-20                                | 0.314 |
|              | 285.0      | 4.09E-20                                | 0.305 | 286.0      | 2.42E-20                                | 0.296 |
|              | 287.0      | 1.22E-20                                | 0.287 | 288.0      | 2.19E-20                                | 0.278 |
|              | 289.0      | 3.14E-20                                | 0.269 | 290.0      | 1.54E-20                                | 0.260 |
|              | 291.0      | 1.49E-20                                | 0.256 | 292.0      | 9.59E-21                                | 0.252 |
|              | 293.0      | 3.22E-20                                | 0.248 | 294.0      | 5.45E-20                                | 0.244 |
|              | 295.0      | 4.07E-20                                | 0.240 | 296.0      | 2.41E-20                                | 0.236 |
|              | 297.0      | 1.79E-20                                | 0.232 | 298.0      | 3.16E-20                                | 0.228 |
|              | 299.0      | 2.81E-20                                | 0.224 | 300.0      | 1.14E-20                                | 0.220 |
|              | 301.0      | 1.27E-20                                | 0.221 | 302.0      | 1.21E-20                                | 0.222 |
|              | 303.0      | 2.78E-20                                | 0.223 | 304.0      | 5.40E-20                                | 0.224 |
|              | 305.0      | 5.30E-20                                | 0.225 | 306.0      | 4.13E-20                                | 0.226 |
|              | 307.0      | 2.23E-20                                | 0.227 | 308.0      | 1.77E-20                                | 0.228 |
|              | 309.0      | 2.43E-20                                | 0.229 | 310.0      | 2.00E-20                                | 0.230 |
|              | 311.0      | 9.15E-21                                | 0.245 | 312.0      | 1.05E-20                                | 0.260 |
|              | 313.0      | 1.43E-20                                | 0.275 | 314.0      | 3.07E-20                                | 0.290 |
|              | 315.0      | 4.50E-20                                | 0.305 | 316.0      | 3.29E-20                                | 0.320 |
|              | 317.0      | 3.77E-20                                | 0.335 | 318.0      | 3.10E-20                                | 0.350 |

(continued)

Table 3 (continued) - 6

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
|              | 319.0      | 1.22E-20                   | 0.365 | 320.0      | 1.26E-20                   | 0.380 |
|              | 321.0      | 1.48E-20                   | 0.411 | 322.0      | 7.70E-21                   | 0.442 |
|              | 323.0      | 4.66E-21                   | 0.473 | 324.0      | 7.11E-21                   | 0.504 |
|              | 325.0      | 1.51E-20                   | 0.535 | 326.0      | 3.90E-20                   | 0.566 |
|              | 327.0      | 3.50E-20                   | 0.597 | 328.0      | 1.49E-20                   | 0.628 |
|              | 329.0      | 2.30E-20                   | 0.659 | 330.0      | 3.05E-20                   | 0.690 |
|              | 331.0      | 1.43E-20                   | 0.690 | 332.0      | 4.22E-21                   | 0.690 |
|              | 333.0      | 2.01E-21                   | 0.690 | 334.0      | 1.66E-21                   | 0.690 |
|              | 335.0      | 9.68E-22                   | 0.690 | 336.0      | 1.57E-21                   | 0.690 |
|              | 337.0      | 3.27E-21                   | 0.690 | 338.0      | 1.38E-20                   | 0.690 |
|              | 339.0      | 3.18E-20                   | 0.690 | 340.0      | 2.39E-20                   | 0.690 |
|              | 341.0      | 8.91E-21                   | 0.661 | 342.0      | 6.91E-21                   | 0.632 |
|              | 343.0      | 1.40E-20                   | 0.603 | 344.0      | 1.13E-20                   | 0.574 |
|              | 345.0      | 3.94E-21                   | 0.545 | 346.0      | 9.93E-22                   | 0.516 |
|              | 347.0      | 7.18E-22                   | 0.487 | 348.0      | 6.70E-22                   | 0.458 |
|              | 349.0      | 7.21E-22                   | 0.429 | 350.0      | 1.87E-22                   | 0.400 |
|              | 351.0      | 8.57E-22                   | 0.372 | 352.0      | 5.46E-21                   | 0.344 |
|              | 353.0      | 1.39E-20                   | 0.316 | 354.0      | 1.39E-20                   | 0.288 |
|              | 355.0      | 6.64E-21                   | 0.260 | 356.0      | 1.97E-21                   | 0.232 |
|              | 357.0      | 4.27E-22                   | 0.204 | 358.0      | 3.22E-22                   | 0.176 |
|              | 359.0      | 2.57E-22                   | 0.148 | 360.0      | 3.73E-22                   | 0.120 |
| CCHOR        | 260.0      | 2.00E-20                   | 0.310 | 270.0      | 3.40E-20                   | 0.390 |
|              | 280.0      | 4.50E-20                   | 0.580 | 290.0      | 4.90E-20                   | 0.530 |
|              | 295.0      | 4.50E-20                   | 0.480 | 300.0      | 4.30E-20                   | 0.430 |
|              | 305.0      | 3.40E-20                   | 0.370 | 315.0      | 2.10E-20                   | 0.170 |
|              | 320.0      | 1.80E-20                   | 0.100 | 325.0      | 1.10E-20                   | 0.040 |
|              | 330.0      | 6.90E-21                   | 0.000 |            |                            |       |
| RCHO         | 280.0      | 5.26E-20                   | 0.960 | 290.0      | 5.77E-20                   | 0.910 |
|              | 300.0      | 5.05E-20                   | 0.860 | 310.0      | 3.68E-20                   | 0.600 |
|              | 320.0      | 1.66E-20                   | 0.360 | 330.0      | 6.49E-21                   | 0.200 |
|              | 340.0      | 1.44E-21                   | 0.080 | 345.0      | 0.00E-01                   | 0.020 |
| ACETONE      | 279.8      | 5.30E-20                   | 0.560 | 283.7      | 5.30E-20                   | 0.460 |
|              | 287.8      | 5.10E-20                   | 0.360 | 292.0      | 4.40E-20                   | 0.250 |
|              | 296.3      | 3.50E-20                   | 0.210 | 300.5      | 3.00E-20                   | 0.150 |
|              | 303.0      | 2.80E-20                   | 0.120 | 304.0      | 2.50E-20                   | 0.110 |
|              | 305.0      | 2.30E-20                   | 0.100 | 306.0      | 2.10E-20                   | 0.090 |
|              | 307.0      | 2.00E-20                   | 0.080 | 308.0      | 1.80E-20                   | 0.070 |
|              | 309.0      | 1.70E-20                   | 0.060 | 310.0      | 1.50E-20                   | 0.050 |
|              | 311.0      | 1.40E-20                   | 0.048 | 312.0      | 1.30E-20                   | 0.046 |
|              | 313.0      | 1.20E-20                   | 0.043 | 314.0      | 1.10E-20                   | 0.041 |
|              | 316.0      | 9.20E-21                   | 0.037 | 320.0      | 5.30E-21                   | 0.028 |
|              | 325.0      | 2.80E-21                   | 0.031 | 330.0      | 1.90E-21                   | 0.033 |
|              | 335.0      | 0.00E-01                   | 0.036 |            |                            |       |

(continued)

Table 3 (continued) - 7

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
| KETONE       | 210.0      | 1.10E-21                   | 1.000 | 220.0      | 1.20E-21                   | 1.000 |
|              | 230.0      | 4.60E-21                   | 1.000 | 240.0      | 1.30E-20                   | 1.000 |
|              | 250.0      | 2.68E-20                   | 1.000 | 260.0      | 4.21E-20                   | 1.000 |
|              | 270.0      | 5.54E-20                   | 1.000 | 280.0      | 5.92E-20                   | 1.000 |
|              | 290.0      | 5.16E-20                   | 1.000 | 300.0      | 3.44E-20                   | 1.000 |
|              | 310.0      | 1.53E-20                   | 1.000 | 320.0      | 4.60E-21                   | 1.000 |
|              | 330.0      | 1.10E-21                   | 1.000 | 340.0      | 0.00E-01                   | 1.000 |
| GLYOXAL1     | 230.0      | 2.87E-21                   | 1.000 | 235.0      | 2.87E-21                   | 1.000 |
|              | 240.0      | 4.30E-21                   | 1.000 | 245.0      | 5.73E-21                   | 1.000 |
|              | 250.0      | 8.60E-21                   | 1.000 | 255.0      | 1.15E-20                   | 1.000 |
|              | 260.0      | 1.43E-20                   | 1.000 | 265.0      | 1.86E-20                   | 1.000 |
|              | 270.0      | 2.29E-20                   | 1.000 | 275.0      | 2.58E-20                   | 1.000 |
|              | 280.0      | 2.87E-20                   | 1.000 | 285.0      | 3.30E-20                   | 1.000 |
|              | 290.0      | 3.15E-20                   | 1.000 | 295.0      | 3.30E-20                   | 1.000 |
|              | 300.0      | 3.58E-20                   | 1.000 | 305.0      | 2.72E-20                   | 1.000 |
|              | 310.0      | 2.72E-20                   | 1.000 | 312.5      | 2.87E-20                   | 1.000 |
|              | 315.0      | 2.29E-20                   | 1.000 | 320.0      | 1.43E-20                   | 1.000 |
|              | 325.0      | 1.15E-20                   | 1.000 | 327.5      | 1.43E-20                   | 1.000 |
|              | 330.0      | 1.15E-20                   | 1.000 | 335.0      | 2.87E-21                   | 1.000 |
|              | 340.0      | 0.00E-01                   | 1.000 |            |                            |       |
| GLYOXAL2     | 355.0      | 0.00E-01                   | 1.000 | 360.0      | 2.29E-21                   | 1.000 |
|              | 365.0      | 2.87E-21                   | 1.000 | 370.0      | 8.03E-21                   | 1.000 |
|              | 375.0      | 1.00E-20                   | 1.000 | 380.0      | 1.72E-20                   | 1.000 |
|              | 382.0      | 1.58E-20                   | 1.000 | 384.0      | 1.49E-20                   | 1.000 |
|              | 386.0      | 1.49E-20                   | 1.000 | 388.0      | 2.87E-20                   | 1.000 |
|              | 390.0      | 3.15E-20                   | 1.000 | 391.0      | 3.24E-20                   | 1.000 |
|              | 392.0      | 3.04E-20                   | 1.000 | 393.0      | 2.23E-20                   | 1.000 |
|              | 394.0      | 2.63E-20                   | 1.000 | 395.0      | 3.04E-20                   | 1.000 |
|              | 396.0      | 2.63E-20                   | 1.000 | 397.0      | 2.43E-20                   | 1.000 |
|              | 398.0      | 3.24E-20                   | 1.000 | 399.0      | 3.04E-20                   | 1.000 |
|              | 400.0      | 2.84E-20                   | 1.000 | 401.0      | 3.24E-20                   | 1.000 |
|              | 402.0      | 4.46E-20                   | 1.000 | 403.0      | 5.27E-20                   | 1.000 |
|              | 404.0      | 4.26E-20                   | 1.000 | 405.0      | 3.04E-20                   | 1.000 |
|              | 406.0      | 3.04E-20                   | 1.000 | 407.0      | 2.84E-20                   | 1.000 |
|              | 408.0      | 2.43E-20                   | 1.000 | 409.0      | 2.84E-20                   | 1.000 |
|              | 410.0      | 6.08E-20                   | 1.000 | 411.0      | 5.07E-20                   | 1.000 |
|              | 411.5      | 6.08E-20                   | 1.000 | 412.0      | 4.86E-20                   | 1.000 |
|              | 413.0      | 8.31E-20                   | 1.000 | 413.5      | 6.48E-20                   | 1.000 |
|              | 414.0      | 7.50E-20                   | 1.000 | 414.5      | 8.11E-20                   | 1.000 |
|              | 415.0      | 8.11E-20                   | 1.000 | 415.5      | 6.89E-20                   | 1.000 |
|              | 416.0      | 4.26E-20                   | 1.000 | 417.0      | 4.86E-20                   | 1.000 |
|              | 418.0      | 5.88E-20                   | 1.000 | 419.0      | 6.69E-20                   | 1.000 |
|              | 420.0      | 3.85E-20                   | 1.000 | 421.0      | 5.67E-20                   | 1.000 |

(continued)

Table 3 (continued) - 8

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>-2</sup> ) | QY    |
|--------------|------------|----------------------------|-------|------------|----------------------------|-------|
|              | 421.5      | 4.46E-20                   | 1.000 | 422.0      | 5.27E-20                   | 1.000 |
|              | 422.5      | 1.05E-19                   | 1.000 | 423.0      | 8.51E-20                   | 1.000 |
|              | 424.0      | 6.08E-20                   | 1.000 | 425.0      | 7.29E-20                   | 1.000 |
|              | 426.0      | 1.18E-19                   | 1.000 | 426.5      | 1.30E-19                   | 1.000 |
|              | 427.0      | 1.07E-19                   | 1.000 | 428.0      | 1.66E-19                   | 1.000 |
|              | 429.0      | 4.05E-20                   | 1.000 | 430.0      | 5.07E-20                   | 1.000 |
|              | 431.0      | 4.86E-20                   | 1.000 | 432.0      | 4.05E-20                   | 1.000 |
|              | 433.0      | 3.65E-20                   | 1.000 | 434.0      | 4.05E-20                   | 1.000 |
|              | 434.5      | 6.08E-20                   | 1.000 | 435.0      | 5.07E-20                   | 1.000 |
|              | 436.0      | 8.11E-20                   | 1.000 | 436.5      | 1.13E-19                   | 1.000 |
|              | 437.0      | 5.27E-20                   | 1.000 | 438.0      | 1.01E-19                   | 1.000 |
|              | 438.5      | 1.38E-19                   | 1.000 | 439.0      | 7.70E-20                   | 1.000 |
|              | 440.0      | 2.47E-19                   | 1.000 | 441.0      | 8.11E-20                   | 1.000 |
|              | 442.0      | 6.08E-20                   | 1.000 | 443.0      | 7.50E-20                   | 1.000 |
|              | 444.0      | 9.32E-20                   | 1.000 | 445.0      | 1.13E-19                   | 1.000 |
|              | 446.0      | 5.27E-20                   | 1.000 | 447.0      | 2.43E-20                   | 1.000 |
|              | 448.0      | 2.84E-20                   | 1.000 | 449.0      | 3.85E-20                   | 1.000 |
|              | 450.0      | 6.08E-20                   | 1.000 | 451.0      | 1.09E-19                   | 1.000 |
|              | 451.5      | 9.32E-20                   | 1.000 | 452.0      | 1.22E-19                   | 1.000 |
|              | 453.0      | 2.39E-19                   | 1.000 | 454.0      | 1.70E-19                   | 1.000 |
|              | 455.0      | 3.40E-19                   | 1.000 | 455.5      | 4.05E-19                   | 1.000 |
|              | 456.0      | 1.01E-19                   | 1.000 | 457.0      | 1.62E-20                   | 1.000 |
|              | 458.0      | 1.22E-20                   | 1.000 | 458.5      | 1.42E-20                   | 1.000 |
|              | 459.0      | 4.05E-21                   | 1.000 | 460.0      | 4.05E-21                   | 1.000 |
|              | 460.5      | 6.08E-21                   | 1.000 | 461.0      | 2.03E-21                   | 1.000 |
|              | 462.0      | 0.00E-01                   | 1.000 |            |                            |       |
| MEGLYOX1     | 220.0      | 2.10E-21                   | 1.000 | 225.0      | 2.10E-21                   | 1.000 |
|              | 230.0      | 4.21E-21                   | 1.000 | 235.0      | 7.57E-21                   | 1.000 |
|              | 240.0      | 9.25E-21                   | 1.000 | 245.0      | 8.41E-21                   | 1.000 |
|              | 250.0      | 9.25E-21                   | 1.000 | 255.0      | 9.25E-21                   | 1.000 |
|              | 260.0      | 9.67E-21                   | 1.000 | 265.0      | 1.05E-20                   | 1.000 |
|              | 270.0      | 1.26E-20                   | 1.000 | 275.0      | 1.43E-20                   | 1.000 |
|              | 280.0      | 1.51E-20                   | 1.000 | 285.0      | 1.43E-20                   | 1.000 |
|              | 290.0      | 1.47E-20                   | 1.000 | 295.0      | 1.18E-20                   | 1.000 |
|              | 300.0      | 1.14E-20                   | 1.000 | 305.0      | 9.25E-21                   | 1.000 |
|              | 310.0      | 6.31E-21                   | 1.000 | 315.0      | 5.47E-21                   | 1.000 |
|              | 320.0      | 3.36E-21                   | 1.000 | 325.0      | 1.68E-21                   | 1.000 |
|              | 330.0      | 8.41E-22                   | 1.000 | 335.0      | 0.00E-01                   | 1.000 |
| MEGLYOX2     | 350.0      | 0.00E-01                   | 1.000 | 354.0      | 4.21E-22                   | 1.000 |
|              | 358.0      | 1.26E-21                   | 1.000 | 360.0      | 2.10E-21                   | 1.000 |
|              | 362.0      | 2.10E-21                   | 1.000 | 364.0      | 2.94E-21                   | 1.000 |
|              | 366.0      | 3.36E-21                   | 1.000 | 368.0      | 4.21E-21                   | 1.000 |
|              | 370.0      | 5.47E-21                   | 1.000 | 372.0      | 5.89E-21                   | 1.000 |

(continued)

Table 3 (continued) - 9

| PHOT<br>Name | WL<br>(nm) | Abs <sub>S</sub><br>(cm <sup>2</sup> ) | QY    | WL<br>(nm)         | Abs <sub>S</sub><br>(cm <sup>2</sup> ) | QY    |
|--------------|------------|--|-------|--------------------|--|-------|
|              | 374.0      | 7.57E-21                               | 1.000 | 376.0              | 7.99E-21                               | 1.000 |
|              | 378.0      | 8.83E-21                               | 1.000 | 380.0              | 1.01E-20                               | 1.000 |
|              | 382.0      | 1.09E-20                               | 1.000 | 384.0              | 1.35E-20                               | 1.000 |
|              | 386.0      | 1.51E-20                               | 1.000 | 388.0              | 1.72E-20                               | 1.000 |
|              | 390.0      | 2.06E-20                               | 1.000 | 392.0              | 2.10E-20                               | 1.000 |
|              | 394.0      | 2.31E-20                               | 1.000 | 396.0              | 2.48E-20                               | 1.000 |
|              | 398.0      | 2.61E-20                               | 1.000 | 400.0              | 2.78E-20                               | 1.000 |
|              | 402.0      | 2.99E-20                               | 1.000 | 404.0              | 3.20E-20                               | 1.000 |
|              | 406.0      | 3.79E-20                               | 1.000 | 408.0              | 3.95E-20                               | 1.000 |
|              | 410.0      | 4.33E-20                               | 1.000 | 412.0              | 4.71E-20                               | 1.000 |
|              | 414.0      | 4.79E-20                               | 1.000 | 416.0              | 4.88E-20                               | 1.000 |
|              | 418.0      | 5.05E-20                               | 1.000 | 420.0              | 5.21E-20                               | 1.000 |
|              | 422.0      | 5.30E-20                               | 1.000 | 424.0              | 5.17E-20                               | 1.000 |
|              | 426.0      | 5.30E-20                               | 1.000 | 428.0              | 5.21E-20                               | 1.000 |
|              | 430.0      | 5.55E-20                               | 1.000 | 432.0              | 5.13E-20                               | 1.000 |
|              | 434.0      | 5.68E-20                               | 1.000 | 436.0              | 6.22E-20                               | 1.000 |
|              | 438.0      | 6.06E-20                               | 1.000 | 440.0              | 5.47E-20                               | 1.000 |
|              | 441.0      | 6.14E-20                               | 1.000 | 442.0              | 5.47E-20                               | 1.000 |
|              | 443.0      | 5.55E-20                               | 1.000 | 443.5 <sup>a</sup> | 6.81E-20                               | 1.000 |
|              | 444.0      | 5.97E-20                               | 1.000 | 445.0              | 5.13E-20                               | 1.000 |
|              | 446.0      | 4.88E-20                               | 1.000 | 447.0              | 5.72E-20                               | 1.000 |
|              | 448.0      | 5.47E-20                               | 1.000 | 449.0              | 6.56E-20                               | 1.000 |
|              | 450.0      | 5.05E-20                               | 1.000 | 451.0              | 3.03E-20                               | 1.000 |
|              | 452.0      | 4.29E-20                               | 1.000 | 453.0              | 2.78E-20                               | 1.000 |
|              | 454.0      | 2.27E-20                               | 1.000 | 456.0              | 1.77E-20                               | 1.000 |
|              | 458.0      | 8.41E-21                               | 1.000 | 460.0              | 4.21E-21                               | 1.000 |
|              | 464.0      | 1.68E-21                               | 1.000 | 468.0              | 0.00E-01                               | 1.000 |
| BZCHO        | 299.0      | 1.78E-19                               | 1.000 | 304.0              | 7.40E-20                               | 1.000 |
|              | 306.0      | 6.91E-20                               | 1.000 | 309.0              | 6.41E-20                               | 1.000 |
|              | 313.0      | 6.91E-20                               | 1.000 | 314.0              | 6.91E-20                               | 1.000 |
|              | 318.0      | 6.41E-20                               | 1.000 | 325.0              | 8.39E-20                               | 1.000 |
|              | 332.0      | 7.65E-20                               | 1.000 | 338.0              | 8.88E-20                               | 1.000 |
|              | 342.0      | 8.88E-20                               | 1.000 | 346.0              | 7.89E-20                               | 1.000 |
|              | 349.0      | 7.89E-20                               | 1.000 | 354.0              | 9.13E-20                               | 1.000 |
|              | 355.0      | 8.14E-20                               | 1.000 | 364.0              | 5.67E-20                               | 1.000 |
|              | 368.0      | 6.66E-20                               | 1.000 | 369.0              | 8.39E-20                               | 1.000 |
|              | 370.0      | 8.39E-20                               | 1.000 | 372.0              | 3.45E-20                               | 1.000 |
|              | 374.0      | 3.21E-20                               | 1.000 | 376.0              | 2.47E-20                               | 1.000 |
|              | 377.0      | 2.47E-20                               | 1.000 | 380.0              | 3.58E-20                               | 1.000 |
|              | 382.0      | 9.90E-21                               | 1.000 | 386.0              | 0.00E-01                               | 1.000 |
| AROMUNKN     | 200.0      | 7.90E-20                               | 1.000 | 350.0              | 7.90E-20                               | 1.000 |
|              | 360.0      | 0.00E-01                               | 1.000 |                    |  |       |

(continued)

Table 3 (continued) - 10

| PHOT<br>Name | WL<br>(nm) | Abs<br>(cm <sup>2</sup> ) | QY    | WL<br>(nm) | Abs<br>(cm <sup>2</sup> ) | QY    |
|--------------|------------|---------------------------|-------|------------|---------------------------|-------|
| CO2H         | 210.0      | 3.75E-19                  | 1.000 | 220.0      | 2.20E-19                  | 1.000 |
|              | 230.0      | 1.38E-19                  | 1.000 | 240.0      | 8.80E-20                  | 1.000 |
|              | 250.0      | 5.80E-20                  | 1.000 | 260.0      | 3.80E-20                  | 1.000 |
|              | 270.0      | 2.50E-20                  | 1.000 | 280.0      | 1.50E-20                  | 1.000 |
|              | 290.0      | 9.00E-21                  | 1.000 | 300.0      | 5.80E-21                  | 1.000 |
|              | 310.0      | 3.40E-21                  | 1.000 | 320.0      | 1.90E-21                  | 1.000 |
|              | 330.0      | 1.10E-21                  | 1.000 | 340.0      | 6.00E-22                  | 1.000 |
|              | 350.0      | 4.00E-22                  | 1.000 | 360.0      | 0.00E-01                  | 1.000 |

<sup>a</sup>When the mechanism test calculations described in this report were carried out, the computer file containing the absorption cross section and quantum yield data for MEGLYOX2 erroneously had a wavelength value of 433.5 where it should have been 443.5. This resulted in our software calculating the photolysis rate for this process being approximately 0.8% high for a direct overhead sum, or 0.1% high for the light source used in the SAPRC Indoor Teflon Chamber. This error was discovered after all the calculations were carried out, and was judged to have too small an effect to justify repeating the calculations. We thank Dr. Harvey Jeffries of the University of North Carolina for pointing out this error.

Table 4. Description of Kinetic and Mechanistic Parameters Used  
in the Generalized Alkane and Aromatic Reaction Mechanism  
(Parameters shown are for reactions of the generalized  
alkane/aromatic species AAR<sub>n</sub>, as listed in Table 2)

| Parameter  | Meaning   |
|--|---|
| <b>KINETIC PARAMETERS</b>  |   |
| kAnOH  | Rate constant for reaction with OH radicals   |
| <b>MECHANISTIC PARAMETERS AFFECTING RADICALS AND/OR NO<sub>x</sub></b> |   |
| AnRR   | Amount of NO to NO <sub>2</sub> conversion with HO <sub>2</sub> formation. (Yield of RO <sub>2</sub> -R.)                                 |
| AnRN   | Amount of reaction with NO to form reactive alkyl nitrates. (Yield of RO <sub>2</sub> -N.)  |
| AnXN   | Amount of reaction with NO to form unreactive nitrates. (Yield of RO <sub>2</sub> -XN.)   |
| AnNP   | Amount of reaction with NO to form aromatic nitro compounds. (Yield of RO <sub>2</sub> -NP.)  |
| AnRH   | Direct HO <sub>2</sub> yield, with no NO to NO <sub>2</sub> conversion.   |
| AnR2   | Amount of extra NO to NO <sub>2</sub> conversion caused by secondarily formed peroxy radicals. (Yield of R <sub>2</sub> O <sub>2</sub> .) |
| <b>ORGANIC PRODUCT YIELD PARAMETERS</b>                                |   |
| AnA1   | Yield of formaldehyde (HCHO)  |
| AnA2   | Yield of acetaldehyde (CCHO)  |
| AnA3   | Yield of propionaldehyde and higher aldehydes (RCHO)  |
| AnK3   | Yield of acetone (ACET)   |
| AnK4   | Yield of higher ketones (MEK)   |
| AnCO   | Yield of CO   |
| AnC2   | Yield of CO <sub>2</sub>  |
| AnPH   | Yield of phenol (PHEN)  |
| AnCR   | Yield of cresols or alkyl phenols (CRES)  |
| AnBZ   | Yield of aromatic aldehydes (BALD)  |
| AnGL   | Yield of glyoxal (GLY)  |
| AnMG   | Yield of methyl glyoxal (MGLY)  |
| AnU1   | Yield of unknown aromatic ring fragmentation product #1 (AFG1)  |
| AnU2   | Yield of unknown aromatic ring fragmentation product #2 (AFG2)  |
| AnNC   | Number of carbons in the alkane, aromatic, or mixture being represented by AAR <sub>n</sub> .   |

(continued)

Table 4 (continued) - 2

| Parameter                                    | Meaning   |
|--|---|
| PARAMETERS DERIVED FROM THE ABOVE PARAMETERS |   |
| AnRO2  | Total peroxy radical (RO2.) yield<br>= AnRR + AnRR + AnNR + AnNP + AnXN + AnR2  |
| AnXN   | "Lost" carbon in OH radical reaction. (Yield of -C.)<br>= AnNC - 5 AnNR - 6 AnNP - AnA1 - 2 AnA2 - 3 AnA3<br>- 4 AnK4 - AnCO - AnC2 - 6 AnPH - 7 AnCR - 7 AnBZ<br>- 2 AnGL - 3 AnMG - 2 AnU1 - 3 AnU2 |

Table 5. Description of Kinetic and Mechanistic Parameters Used in the Generalized Alkene Reaction Mechanism (Parameters shown are for reactions of the generalized alkene species OLEn)

| Parameter  | Meaning  |  |
|--|--|--|
| <b>KINETIC PARAMETERS</b>  |  |  |
| kOnOH  | Rate constant for reaction with OH radicals  |  |
| kOnO3  | Rate constant for reaction with ozone  |  |
| kOnN3  | Rate constant for reaction with NO <sub>3</sub> radicals                             |  |
| kOnOA  | Rate constant for reaction with O( <sup>3</sup> P) atoms                             |  |
| <b>STRUCTURAL PARAMETERS GIVING GROUPS ABOUT THE MOST REACTIVE DOUBLE BOND</b> |  |  |
| OnP1   | Number of =CH <sub>2</sub> groups  |  |
| OnP2   | Number of =CHCH <sub>3</sub> groups  |  |
| OnP3   | Number of =CHR groups, where R not H or CH <sub>3</sub>                              |  |
| OnP4   | Number of =C(CH <sub>3</sub> ) <sub>2</sub> groups                                   |  |
| OnP5   | Number of =C(CH <sub>3</sub> ) <sub>2</sub> (R) or =CR <sub>2</sub> groups           |  |
| <b>OTHER MECHANISTIC PARAMETERS</b>  |  |  |
| OnPN   | Organic nitrate yield in the OH reaction. (Yield of RO <sub>2</sub> -N.)             |  |
| OnGA   | Glycolaldehyde (CCHO) yield in the OH reaction                                       |  |
| OnNC   | Number of carbons in the alkene, or average number of carbons in the alkene mixture. |  |
| <b>PRODUCT YIELD PARAMETERS DERIVED FROM THE ABOVE PARAMETERS</b>              |  |  |
| Rxn.   | Product  | Derivation   |
| OnPR   | OH   | RO <sub>2</sub> -R.  |
| OnP1R  |  | 1 - OnPN   |
| OnP2R  | HCHO   | ( OnPR x OnPN ) - 2 OnGA   |
| OnP3R  | CCHO   | ( OnPN x OnP2 ) + OnGA   |
| OnP4R  | RCHO   | OnPN x OnP3  |
| OnP5R  | ACET   | OnPN x OnP4  |
| OnOHXC   | MEK  | OnPN x OnP5  |
|  | Lost C   | OnNC - OnP1R - 2 OnP2R - 3 OnP3R - 3 OnP4R<br>- 4 OnP5R - 5 OnPN |
| OnO3A1   | O3   | HCHO   |
| OnO3A2   |  | 0.5 ( OnP1 + 0.3 OnP2 + 0.1 OnP5 )                               |
| OnO3A3   | CCHO   | 0.5 ( OnP2 + 0.3 OnP3 + 0.1 OnP5 )                               |
| OnO3K3   | RCHO   | 0.5 OnP3   |
| OnO3K4   | ACET   | 0.5 OnP4   |
|  | MEK  | 0.5 ( 0.28 OnP2 + 0.42 OnP3 + 0.8 OnP4<br>+ 0.8 OnP5 )           |
| OnO3MG   | MGLY   | 0.5 ( 0.2 OnP4 )   |
| OnO3CO   | CO   | 0.5 ( 0.44 OnP1 + 0.15 OnP2 + 0.15 OnP3 )                        |

(continued)

Table 5 (continued) - 2

| Parameter | Meaning | Rxn.   | Product  | Derivation  |
|-----------|---------|--------|----------|---|
| OnO3SB    |         |        | O3OL-SB  | 0.5 ( 0.37 OnP1 + 0.2 OnP2 + 0.2 OnP3)  |
| OnO3P1    |         |        | CCO-02.  | 0.5 ( 0.1 OnP5)   |
| OnO3P2    |         |        | C2CO-02. | 0.5 ( 0.1 OnP5)   |
| OnO3RH    |         |        | H02.     | 0.5 ( 0.12 OnP1 + 0.21 OnP2 + 0.21 OnP3)  |
| OnO3OH    |         |        | HO.      | 0.5 ( 0.12 OnP2 + 0.12 OnP3 + 0.2 OnP4<br>+ 0.2 OnP5)   |
| OnO3RR    |         |        | R02-R.   | 0.5 ( 0.27 OnP2 + 0.27 OnP3 + 0.2 OnP4)   |
| OnO3R2    |         |        | R2O2.    | 0.5 ( 0.3 OnP5)   |
| OnO3R02   |         |        | R02.     | OnO3RR + OnO3R2   |
| OnO3PS    |         |        | RCO3.    | OnO3P1 + OnO3P2   |
| OnO3XN    |         |        | Lost C   | OnNC - OnO3A1 - 2 OnO3A2 - 3 OnO3A3<br>- 3 OnO3K3 - 4 OnO3K4 - 3 OnO3MG - OnO3CO<br>- 2 OnO3P1 - 3 OnO3P2 |
| OnOAXC    | O       | Lost C |          | OnNC - 3.5  |
| OnN3XC    | N03     | Lost C |          | OnNC - OnP1 - 2 OnP2 - 3 OnP3 - 3 OnP4<br>- 4 OnP5  |

Table 6. Listing of Kinetic and Mechanistic Parameters Assigned for the Alkane Detailed Model  
 Species (Parameters are given for T = 300, 270, and 330 K. Parameters for intermediate temperatures are obtained by linear interpolation)

| Name                 | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       |       |       |       |       |       |
|----------------------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                      |                  | RR                                    | NR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | C0    | C2    |
| T = 300. K           |                  |                                       |       |       |       |       |       |       |       |       |       |       |
| METHANE <sup>c</sup> | 8.77E-15         | 1.000                                 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ETHANE <sup>d</sup>  | 2.81E-13         | 1.000                                 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| PROPANE <sup>e</sup> | 1.22E-12         | 0.961                                 | 0.000 | 0.039 | 0.000 | 0.000 | 0.303 | 0.658 | 0.000 | 0.000 | 0.000 | 0.000 |
| N-C4                 | 2.56E-12         | 0.924                                 | 0.076 | 0.000 | 0.397 | 0.001 | 0.571 | 0.140 | 0.000 | 0.533 | 0.000 | 0.000 |
| N-C5                 | 3.96E-12         | 0.880                                 | 0.120 | 0.000 | 0.544 | 0.007 | 0.080 | 0.172 | 0.000 | 0.929 | 0.000 | 0.000 |
| N-C6                 | 5.36E-12         | 0.815                                 | 0.185 | 0.000 | 0.738 | 0.000 | 0.020 | 0.105 | 0.000 | 1.134 | 0.000 | 0.000 |
| N-C7                 | 6.76E-12         | 0.733                                 | 0.267 | 0.000 | 0.727 | 0.000 | 0.000 | 0.056 | 0.000 | 1.241 | 0.000 | 0.000 |
| N-C8                 | 8.16E-12         | 0.667                                 | 0.333 | 0.000 | 0.706 | 0.000 | 0.000 | 0.002 | 0.000 | 1.333 | 0.000 | 0.000 |
| N-C9                 | 9.56E-12         | 0.627                                 | 0.373 | 0.000 | 0.673 | 0.000 | 0.000 | 0.001 | 0.000 | 1.299 | 0.000 | 0.000 |
| N-C10                | 1.10E-11         | 0.603                                 | 0.397 | 0.000 | 0.659 | 0.000 | 0.000 | 0.001 | 0.000 | 1.261 | 0.000 | 0.000 |
| N-C11                | 1.24E-11         | 0.589                                 | 0.411 | 0.000 | 0.654 | 0.000 | 0.000 | 0.001 | 0.000 | 1.241 | 0.000 | 0.000 |
| N-C12                | 1.38E-11         | 0.580                                 | 0.420 | 0.000 | 0.644 | 0.000 | 0.000 | 0.001 | 0.000 | 1.223 | 0.000 | 0.000 |
| N-C13                | 1.52E-11         | 0.573                                 | 0.427 | 0.000 | 0.638 | 0.000 | 0.000 | 0.001 | 0.000 | 1.211 | 0.000 | 0.000 |
| N-C14                | 1.66E-11         | 0.569                                 | 0.431 | 0.000 | 0.634 | 0.000 | 0.000 | 0.001 | 0.000 | 1.202 | 0.000 | 0.000 |
| N-C15                | 1.80E-11         | 0.566                                 | 0.434 | 0.000 | 0.631 | 0.000 | 0.000 | 0.001 | 0.000 | 1.196 | 0.000 | 0.000 |
| ISO-C4               | 2.39E-12         | 0.973                                 | 0.027 | 0.000 | 0.744 | 0.000 | 0.000 | 0.229 | 0.744 | 0.000 | 0.000 | 0.000 |
| ISO-C5               | 4.00E-12         | 0.933                                 | 0.064 | 0.002 | 0.734 | 0.000 | 0.614 | 0.133 | 0.611 | 0.303 | 0.000 | 0.000 |
| BR-C5                | 4.00E-12         | 0.933                                 | 0.064 | 0.002 | 0.734 | 0.000 | 0.614 | 0.133 | 0.611 | 0.303 | 0.000 | 0.000 |
| NEO-C5               | 7.55E-13         | 0.949                                 | 0.051 | 0.000 | 0.019 | 0.019 | 0.000 | 0.939 | 0.010 | 0.000 | 0.000 | 0.000 |
| 2-ME-C5              | 5.40E-12         | 0.873                                 | 0.122 | 0.005 | 0.749 | 0.006 | 0.023 | 0.545 | 0.223 | 0.724 | 0.000 | 0.000 |
| 3-ME-C5              | 5.76E-12         | 0.888                                 | 0.112 | 0.000 | 0.860 | 0.005 | 0.523 | 0.089 | 0.000 | 1.003 | 0.000 | 0.000 |
| 22-DMB               | 1.84E-12         | 0.847                                 | 0.153 | 0.000 | 0.960 | 0.295 | 0.303 | 0.372 | 0.295 | 0.542 | 0.000 | 0.000 |
| 23-DMB               | 5.44E-12         | 0.901                                 | 0.061 | 0.039 | 0.944 | 0.000 | 0.000 | 0.128 | 1.584 | 0.096 | 0.000 | 0.000 |
| 4-ME-C6              | 7.16E-12         | 0.815                                 | 0.182 | 0.002 | 0.842 | 0.000 | 0.127 | 0.329 | 0.000 | 1.119 | 0.000 | 0.000 |
| 24-DM-C5             | 6.84E-12         | 0.867                                 | 0.131 | 0.002 | 0.844 | 0.000 | 0.000 | 0.772 | 0.257 | 0.682 | 0.000 | 0.000 |
| 23-DM-C5             | 7.21E-12         | 0.860                                 | 0.128 | 0.011 | 1.101 | 0.036 | 0.253 | 0.185 | 0.390 | 0.960 | 0.000 | 0.000 |
| ISO-C8               | 4.69E-12         | 0.811                                 | 0.188 | 0.001 | 0.942 | 0.111 | 0.000 | 0.747 | 0.251 | 0.643 | 0.000 | 0.000 |
| CYCC5                | 5.62E-12         | 0.873                                 | 0.127 | 0.000 | 1.745 | 0.000 | 0.000 | 0.873 | 0.000 | 0.218 | 0.873 | 0.000 |
| ME-CYCC5             | 7.10E-12         | 0.856                                 | 0.144 | 0.000 | 2.057 | 0.321 | 0.000 | 0.622 | 0.000 | 0.550 | 0.535 | 0.214 |

(continued)

Table 6 (continued) - 2

| Name     | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       |       |       |       |       |
|----------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|          |                  | RR                                    | MR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | C0    |
| CYCC6    | 8.41E-12         | 0.807                                 | 0.193 | 0.000 | 0.352 | 0.003 | 0.000 | 0.333 | 0.000 | 0.816 | 0.000 |
| ME-CYCC6 | 1.02E-11         | 0.784                                 | 0.216 | 0.000 | 0.977 | 0.100 | 0.001 | 0.474 | 0.000 | 0.979 | 0.003 |
| ET-CYCC6 | 1.22E-11         | 0.737                                 | 0.263 | 0.000 | 1.464 | 0.185 | 0.310 | 0.393 | 0.000 | 0.930 | 0.010 |
| 3-ME-C6  | 7.16E-12         | 0.815                                 | 0.182 | 0.002 | 0.842 | 0.000 | 0.127 | 0.329 | 0.000 | 1.119 | 0.000 |
| 4-ME-C7  | 8.57E-12         | 0.753                                 | 0.244 | 0.002 | 0.803 | 0.000 | 0.000 | 0.352 | 0.000 | 1.204 | 0.000 |
| 4-ET-C7  | 1.05E-11         | 0.727                                 | 0.271 | 0.002 | 0.804 | 0.002 | 0.059 | 0.303 | 0.000 | 1.167 | 0.000 |
| 4-PR-C7  | 1.19E-11         | 0.696                                 | 0.301 | 0.002 | 0.775 | 0.000 | 0.004 | 0.328 | 0.000 | 1.139 | 0.000 |
| BR-C6    | 5.40E-12         | 0.873                                 | 0.122 | 0.005 | 0.749 | 0.006 | 0.023 | 0.545 | 0.223 | 0.724 | 0.000 |
| BR-C7    | 7.16E-12         | 0.815                                 | 0.182 | 0.002 | 0.842 | 0.000 | 0.127 | 0.329 | 0.000 | 1.119 | 0.000 |
| BR-C8    | 8.57E-12         | 0.753                                 | 0.244 | 0.002 | 0.803 | 0.000 | 0.000 | 0.352 | 0.000 | 1.204 | 0.000 |
| BR-C9    | 1.05E-11         | 0.727                                 | 0.271 | 0.002 | 0.804 | 0.002 | 0.059 | 0.303 | 0.000 | 1.167 | 0.000 |
| BR-C10   | 1.19E-11         | 0.696                                 | 0.301 | 0.002 | 0.775 | 0.000 | 0.004 | 0.328 | 0.000 | 1.139 | 0.000 |
| BR-C11   | 1.43E-11         | 0.754                                 | 0.246 | 0.000 | 1.273 | 0.021 | 0.054 | 0.090 | 0.000 | 1.862 | 0.000 |
| BR-C12   | 1.57E-11         | 0.733                                 | 0.267 | 0.000 | 1.350 | 0.002 | 0.422 | 0.012 | 0.000 | 1.647 | 0.000 |
| BR-C13   | 1.71E-11         | 0.715                                 | 0.285 | 0.000 | 1.226 | 0.002 | 0.008 | 0.111 | 0.000 | 1.819 | 0.000 |
| BR-C14   | 1.85E-11         | 0.702                                 | 0.298 | 0.000 | 1.122 | 0.002 | 0.000 | 0.003 | 0.000 | 1.820 | 0.000 |
| BR-C15   | 1.99E-11         | 0.690                                 | 0.310 | 0.000 | 1.103 | 0.001 | 0.000 | 0.003 | 0.000 | 1.790 | 0.000 |
| CYC-C6   | 8.41E-12         | 0.807                                 | 0.193 | 0.000 | 0.352 | 0.003 | 0.000 | 0.333 | 0.000 | 0.816 | 0.000 |
| CYC-C7   | 1.02E-11         | 0.784                                 | 0.216 | 0.000 | 0.977 | 0.100 | 0.001 | 0.474 | 0.000 | 0.979 | 0.003 |
| CYC-C8   | 1.22E-11         | 0.737                                 | 0.263 | 0.000 | 1.464 | 0.185 | 0.310 | 0.393 | 0.000 | 0.930 | 0.010 |
| CYC-C9   | 1.40E-11         | 0.756                                 | 0.244 | 0.000 | 1.970 | 0.283 | 0.264 | 0.502 | 0.000 | 1.056 | 0.000 |
| CYC-C10  | 1.59E-11         | 0.739                                 | 0.261 | 0.000 | 1.874 | 0.208 | 0.390 | 0.228 | 0.000 | 1.359 | 0.011 |
| CYC-C11  | 1.77E-11         | 0.767                                 | 0.233 | 0.000 | 1.855 | 0.236 | 0.376 | 0.144 | 0.000 | 1.464 | 0.001 |
| CYC-C12  | 1.97E-11         | 0.757                                 | 0.243 | 0.000 | 2.040 | 0.202 | 0.437 | 0.110 | 0.000 | 1.708 | 0.001 |
| CYC-C13  | 2.11E-11         | 0.738                                 | 0.261 | 0.000 | 1.638 | 0.104 | 0.243 | 0.198 | 0.000 | 1.649 | 0.002 |
| CYC-C14  | 2.25E-11         | 0.725                                 | 0.274 | 0.001 | 1.498 | 0.069 | 0.070 | 0.439 | 0.000 | 1.516 | 0.002 |
| CYC-C15  | 2.39E-11         | 0.714                                 | 0.283 | 0.002 | 1.611 | 0.040 | 0.027 | 0.465 | 0.000 | 1.719 | 0.002 |
| C4C5f    | 3.22E-12         | 0.927                                 | 0.072 | 0.001 | 0.604 | 0.188 | 0.316 | 0.168 | 0.339 | 0.441 | 0.000 |
| C6PLUSf  | 6.14E-12         | 0.808                                 | 0.184 | 0.008 | 0.844 | 0.022 | 0.042 | 0.252 | 0.350 | 0.876 | 0.000 |

(continued)

Table 6 (continued) - 3

| Name       | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       |       |       |       |       |
|------------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|            |                  | RR                                    | NR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | CO    |
| T = 270. K |                  |                                       |       |       |       |       |       |       |       |       |       |
| METHANE    | 4.42E-15         | 1.000                                 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ETHANE     | 1.93E-13         | 1.000                                 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| PROPANE    | 1.03E-12         | 0.948                                 | 0.000 | 0.052 | 0.000 | 0.000 | 0.267 | 0.681 | 0.000 | 0.000 | 0.000 |
| N-C4       | 2.26E-12         | 0.889                                 | 0.111 | 0.000 | 0.084 | 0.000 | 0.064 | 0.118 | 0.000 | 0.768 | 0.000 |
| N-C5       | 3.57E-12         | 0.816                                 | 0.184 | 0.000 | 0.266 | 0.000 | 0.060 | 0.000 | 0.975 | 0.000 | 0.000 |
| N-C6       | 4.88E-12         | 0.733                                 | 0.267 | 0.000 | 0.513 | 0.000 | 0.042 | 0.000 | 1.068 | 0.000 | 0.000 |
| N-C7       | 6.19E-12         | 0.623                                 | 0.377 | 0.000 | 0.577 | 0.000 | 0.028 | 0.000 | 1.070 | 0.000 | 0.000 |
| N-C8       | 7.50E-12         | 0.517                                 | 0.483 | 0.000 | 0.546 | 0.000 | 0.001 | 0.000 | 1.033 | 0.000 | 0.000 |
| N-C9       | 8.81E-12         | 0.449                                 | 0.551 | 0.000 | 0.480 | 0.000 | 0.001 | 0.000 | 0.929 | 0.000 | 0.000 |
| N-C10      | 1.01E-11         | 0.411                                 | 0.589 | 0.000 | 0.446 | 0.000 | 0.001 | 0.000 | 0.856 | 0.000 | 0.000 |
| N-C11      | 1.14E-11         | 0.390                                 | 0.610 | 0.000 | 0.428 | 0.000 | 0.001 | 0.000 | 0.818 | 0.000 | 0.000 |
| N-C12      | 1.27E-11         | 0.378                                 | 0.622 | 0.000 | 0.414 | 0.000 | 0.000 | 0.000 | 0.792 | 0.000 | 0.000 |
| N-C13      | 1.40E-11         | 0.370                                 | 0.630 | 0.000 | 0.406 | 0.000 | 0.000 | 0.000 | 0.775 | 0.000 | 0.000 |
| N-C14      | 1.54E-11         | 0.364                                 | 0.636 | 0.000 | 0.400 | 0.000 | 0.000 | 0.000 | 0.763 | 0.000 | 0.000 |
| N-C15      | 1.67E-11         | 0.360                                 | 0.640 | 0.000 | 0.395 | 0.000 | 0.000 | 0.000 | 0.755 | 0.000 | 0.000 |
| ISO-C4     | 2.34E-12         | 0.962                                 | 0.038 | 0.000 | 0.790 | 0.000 | 0.172 | 0.790 | 0.000 | 0.000 | 0.000 |
| ISO-C5     | 3.95E-12         | 0.906                                 | 0.094 | 0.000 | 0.662 | 0.000 | 0.609 | 0.098 | 0.609 | 0.250 | 0.000 |
| BR-C5      | 3.95E-12         | 0.906                                 | 0.094 | 0.000 | 0.662 | 0.000 | 0.609 | 0.098 | 0.609 | 0.250 | 0.000 |
| NEO-C5     | 5.62E-13         | 0.923                                 | 0.077 | 0.000 | 0.000 | 0.000 | 0.923 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-ME-C5    | 5.26E-12         | 0.828                                 | 0.170 | 0.003 | 0.615 | 0.004 | 0.000 | 0.496 | 0.102 | 0.795 | 0.000 |
| 3-ME-C5    | 5.76E-12         | 0.848                                 | 0.152 | 0.000 | 0.714 | 0.000 | 0.538 | 0.055 | 0.000 | 0.962 | 0.000 |
| 22-DMB     | 1.55E-12         | 0.782                                 | 0.218 | 0.000 | 0.298 | 0.056 | 0.058 | 0.322 | 0.056 | 0.589 | 0.000 |
| 23-DMB     | 5.64E-12         | 0.863                                 | 0.086 | 0.051 | 0.887 | 0.000 | 0.000 | 0.089 | 1.600 | 0.061 | 0.000 |
| 4-ME-C6    | 7.07E-12         | 0.754                                 | 0.245 | 0.002 | 0.718 | 0.000 | 0.079 | 0.372 | 0.000 | 1.002 | 0.000 |
| 24-DM-C5   | 6.95E-12         | 0.826                                 | 0.174 | 0.000 | 0.737 | 0.000 | 0.000 | 0.715 | 0.091 | 0.757 | 0.000 |
| 23-DM-C5   | 7.46E-12         | 0.818                                 | 0.167 | 0.016 | 0.938 | 0.021 | 0.152 | 0.235 | 0.335 | 0.947 | 0.000 |
| ISO-C8     | 4.55E-12         | 0.741                                 | 0.259 | 0.000 | 0.659 | 0.017 | 0.000 | 0.616 | 0.067 | 0.699 | 0.000 |
| CYCC5      | 5.12E-12         | 0.807                                 | 0.193 | 0.000 | 1.613 | 0.000 | 0.000 | 0.807 | 0.000 | 0.202 | 0.807 |
| ME-CYCC5   | 6.86E-12         | 0.801                                 | 0.199 | 0.000 | 1.971 | 0.351 | 0.000 | 0.579 | 0.000 | 0.509 | 0.448 |
| CYCC6      | 7.86E-12         | 0.724                                 | 0.276 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.724 | 0.000 | 0.000 |
| ME-CYCC6   | 1.00E-11         | 0.707                                 | 0.293 | 0.000 | 0.739 | 0.077 | 0.000 | 0.270 | 0.000 | 1.007 | 0.035 |

(continued)

Table 6 (continued) - 4

| Name       | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       |       |       |       |       |       |
|------------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|            |                  | RR                                    | NR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | CO    | C2    |
| ET-CYCC6   | 1.21E-11         | 0.636                                 | 0.364 | 0.000 | 1.285 | 0.203 | 0.327 | 0.265 | 0.000 | 0.720 | 0.000 | 0.203 |
| 3-ME-C6    | 7.07E-12         | 0.754                                 | 0.245 | 0.002 | 0.718 | 0.000 | 0.079 | 0.372 | 0.000 | 1.002 | 0.000 | 0.000 |
| 4-ME-C7    | 8.38E-12         | 0.658                                 | 0.340 | 0.002 | 0.681 | 0.000 | 0.000 | 0.367 | 0.000 | 0.972 | 0.000 | 0.000 |
| 4-ET-C7    | 1.05E-11         | 0.617                                 | 0.381 | 0.002 | 0.654 | 0.001 | 0.036 | 0.340 | 0.000 | 0.894 | 0.000 | 0.000 |
| 4-PR-C7    | 1.18E-11         | 0.571                                 | 0.427 | 0.002 | 0.604 | 0.000 | 0.001 | 0.338 | 0.000 | 0.836 | 0.000 | 0.000 |
| BR-C6      | 5.26E-12         | 0.828                                 | 0.170 | 0.003 | 0.615 | 0.004 | 0.000 | 0.496 | 0.102 | 0.795 | 0.000 | 0.000 |
| BR-C7      | 7.07E-12         | 0.754                                 | 0.245 | 0.002 | 0.718 | 0.000 | 0.079 | 0.372 | 0.000 | 1.002 | 0.000 | 0.000 |
| BR-C8      | 8.38E-12         | 0.658                                 | 0.340 | 0.002 | 0.681 | 0.000 | 0.000 | 0.367 | 0.000 | 0.972 | 0.000 | 0.000 |
| BR-C9      | 1.05E-11         | 0.617                                 | 0.381 | 0.002 | 0.654 | 0.001 | 0.036 | 0.340 | 0.000 | 0.894 | 0.000 | 0.000 |
| BR-C10     | 1.18E-11         | 0.571                                 | 0.427 | 0.002 | 0.604 | 0.000 | 0.001 | 0.338 | 0.000 | 0.836 | 0.000 | 0.000 |
| BR-C11     | 1.47E-11         | 0.657                                 | 0.343 | 0.000 | 0.920 | 0.004 | 0.010 | 0.032 | 0.000 | 1.530 | 0.000 | 0.000 |
| BR-C12     | 1.60E-11         | 0.628                                 | 0.372 | 0.000 | 1.259 | 0.001 | 0.441 | 0.011 | 0.000 | 1.433 | 0.000 | 0.000 |
| BR-C13     | 1.74E-11         | 0.604                                 | 0.396 | 0.000 | 0.935 | 0.001 | 0.000 | 0.040 | 0.000 | 1.497 | 0.000 | 0.000 |
| BR-C14     | 1.87E-11         | 0.584                                 | 0.416 | 0.000 | 1.000 | 0.001 | 0.000 | 0.001 | 0.000 | 1.582 | 0.000 | 0.000 |
| BR-C15     | 2.00E-11         | 0.566                                 | 0.434 | 0.000 | 0.962 | 0.001 | 0.000 | 0.001 | 0.000 | 1.526 | 0.000 | 0.000 |
| CYC-C6     | 7.86E-12         | 0.724                                 | 0.276 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.724 | 0.000 | 0.000 |
| CYC-C7     | 1.00E-11         | 0.707                                 | 0.293 | 0.000 | 0.739 | 0.077 | 0.000 | 0.270 | 0.000 | 1.007 | 0.000 | 0.035 |
| CYC-C8     | 1.21E-11         | 0.636                                 | 0.364 | 0.000 | 1.285 | 0.203 | 0.327 | 0.265 | 0.000 | 0.720 | 0.000 | 0.203 |
| CYC-C9     | 1.43E-11         | 0.659                                 | 0.341 | 0.000 | 1.794 | 0.288 | 0.269 | 0.399 | 0.000 | 0.910 | 0.000 | 0.273 |
| CYC-C10    | 1.64E-11         | 0.635                                 | 0.365 | 0.000 | 1.685 | 0.216 | 0.388 | 0.145 | 0.000 | 1.136 | 0.093 | 0.216 |
| CYC-C11    | 1.86E-11         | 0.675                                 | 0.325 | 0.000 | 1.579 | 0.204 | 0.335 | 0.035 | 0.000 | 1.298 | 0.000 | 0.188 |
| CYC-C12    | 2.07E-11         | 0.662                                 | 0.338 | 0.000 | 1.781 | 0.174 | 0.384 | 0.036 | 0.000 | 1.506 | 0.000 | 0.171 |
| CYC-C13    | 2.20E-11         | 0.640                                 | 0.359 | 0.000 | 1.314 | 0.076 | 0.195 | 0.062 | 0.000 | 1.467 | 0.001 | 0.074 |
| CYC-C14    | 2.33E-11         | 0.621                                 | 0.378 | 0.001 | 0.998 | 0.034 | 0.024 | 0.314 | 0.000 | 1.175 | 0.001 | 0.032 |
| CYC-C15    | 2.46E-11         | 0.604                                 | 0.394 | 0.002 | 1.156 | 0.024 | 0.013 | 0.428 | 0.000 | 1.246 | 0.001 | 0.024 |
| C4C5       | 3.03E-12         | 0.893                                 | 0.107 | 0.000 | 0.451 | 0.198 | 0.168 | 0.112 | 0.350 | 0.498 | 0.000 | 0.000 |
| C6PLUS     | 5.92E-12         | 0.732                                 | 0.258 | 0.010 | 0.676 | 0.006 | 0.022 | 0.215 | 0.301 | 0.810 | 0.000 | 0.000 |
| T = 330. K |                  |                                       |       |       |       |       |       |       |       |       |       |       |
| METHANE    | 1.56E-14         | 1.000                                 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ETHANE     | 3.89E-13         | 1.000                                 | 0.000 | 0.000 | 1.000 | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| PROPANE    | 1.44E-12         | 0.972                                 | 0.000 | 0.028 | 0.020 | 0.020 | 0.020 | 0.331 | 0.621 | 0.000 | 0.000 | 0.000 |

(continued)

Table 6 (continued) - 5

| Name     | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       |       |       |       |       |       |
|----------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|          |                  | RR                                    | NR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | CO    | C2    |
| N-C4     | 2.89E-12         | 0.950                                 | 0.050 | 0.000 | 0.806 | 0.006 | 1.303 | 0.160 | 0.000 | 0.177 | 0.000 | 0.000 |
| N-C5     | 4.40E-12         | 0.919                                 | 0.081 | 0.001 | 0.817 | 0.014 | 0.274 | 0.385 | 0.000 | 0.719 | 0.000 | 0.000 |
| N-C6     | 5.91E-12         | 0.872                                 | 0.128 | 0.000 | 0.863 | 0.000 | 0.050 | 0.194 | 0.000 | 1.137 | 0.000 | 0.000 |
| N-C7     | 7.42E-12         | 0.825                                 | 0.175 | 0.000 | 0.839 | 0.000 | 0.000 | 0.091 | 0.000 | 1.375 | 0.000 | 0.000 |
| N-C8     | 8.93E-12         | 0.792                                 | 0.208 | 0.000 | 0.839 | 0.000 | 0.000 | 0.003 | 0.000 | 1.582 | 0.000 | 0.000 |
| N-C9     | 1.04E-11         | 0.771                                 | 0.229 | 0.000 | 0.835 | 0.000 | 0.000 | 0.002 | 0.000 | 1.604 | 0.000 | 0.000 |
| N-C10    | 1.20E-11         | 0.759                                 | 0.241 | 0.000 | 0.838 | 0.000 | 0.000 | 0.002 | 0.000 | 1.595 | 0.000 | 0.000 |
| N-C11    | 1.35E-11         | 0.751                                 | 0.249 | 0.000 | 0.846 | 0.000 | 0.000 | 0.002 | 0.000 | 1.595 | 0.000 | 0.000 |
| N-C12    | 1.50E-11         | 0.745                                 | 0.255 | 0.000 | 0.843 | 0.000 | 0.000 | 0.002 | 0.000 | 1.586 | 0.000 | 0.000 |
| N-C13    | 1.65E-11         | 0.742                                 | 0.258 | 0.000 | 0.841 | 0.000 | 0.000 | 0.001 | 0.000 | 1.581 | 0.000 | 0.000 |
| N-C14    | 1.80E-11         | 0.739                                 | 0.261 | 0.000 | 0.840 | 0.000 | 0.000 | 0.001 | 0.000 | 1.577 | 0.000 | 0.000 |
| N-C15    | 1.95E-11         | 0.737                                 | 0.263 | 0.000 | 0.838 | 0.000 | 0.000 | 0.001 | 0.000 | 1.573 | 0.000 | 0.000 |
| ISO-C4   | 2.51E-12         | 0.982                                 | 0.018 | 0.000 | 0.701 | 0.000 | 0.281 | 0.701 | 0.000 | 0.000 | 0.000 | 0.000 |
| ISO-C5   | 4.17E-12         | 0.949                                 | 0.045 | 0.006 | 0.893 | 0.018 | 0.707 | 0.166 | 0.686 | 0.192 | 0.000 | 0.000 |
| BR-C5    | 4.17E-12         | 0.949                                 | 0.045 | 0.006 | 0.893 | 0.018 | 0.707 | 0.166 | 0.686 | 0.192 | 0.000 | 0.000 |
| NEO-C5   | 9.78E-13         | 0.964                                 | 0.036 | 0.000 | 0.202 | 0.000 | 0.864 | 0.100 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-ME-C5  | 5.68E-12         | 0.906                                 | 0.087 | 0.007 | 0.944 | 0.011 | 0.079 | 0.661 | 0.384 | 0.537 | 0.000 | 0.000 |
| 3-ME-C5  | 5.94E-12         | 0.917                                 | 0.083 | 0.000 | 0.988 | 0.013 | 0.595 | 0.118 | 0.000 | 0.988 | 0.000 | 0.000 |
| 22-DMB   | 2.18E-12         | 0.894                                 | 0.106 | 0.000 | 1.377 | 0.045 | 0.452 | 0.414 | 0.445 | 0.363 | 0.000 | 0.000 |
| 23-DMB   | 5.45E-12         | 0.930                                 | 0.043 | 0.027 | 1.008 | 0.020 | 0.020 | 0.170 | 1.527 | 0.127 | 0.000 | 0.000 |
| 4-ME-C6  | 7.45E-12         | 0.874                                 | 0.125 | 0.002 | 0.968 | 0.003 | 0.193 | 0.315 | 0.000 | 1.197 | 0.000 | 0.000 |
| 24-DM-C5 | 6.96E-12         | 0.904                                 | 0.090 | 0.005 | 1.066 | 0.019 | 0.005 | 0.869 | 0.533 | 0.533 | 0.000 | 0.000 |
| 23-DM-C5 | 7.22E-12         | 0.902                                 | 0.090 | 0.008 | 1.267 | 0.054 | 0.489 | 0.158 | 0.433 | 0.893 | 0.000 | 0.000 |
| ISO-C8   | 4.97E-12         | 0.875                                 | 0.124 | 0.001 | 1.306 | 0.268 | 0.001 | 0.824 | 0.502 | 0.586 | 0.000 | 0.000 |
| CYCC5    | 6.17E-12         | 0.913                                 | 0.087 | 0.000 | 1.827 | 0.000 | 0.000 | 0.913 | 0.000 | 0.228 | 0.913 | 0.000 |
| ME-CYCC5 | 7.48E-12         | 0.897                                 | 0.103 | 0.000 | 2.123 | 0.295 | 0.000 | 0.657 | 0.000 | 0.580 | 0.599 | 0.199 |
| CYCC6    | 9.06E-12         | 0.865                                 | 0.135 | 0.000 | 1.313 | 0.031 | 0.000 | 1.223 | 0.000 | 0.365 | 0.015 | 0.017 |
| ME-CYCC6 | 1.06E-11         | 0.854                                 | 0.146 | 0.000 | 1.678 | 0.145 | 0.006 | 0.971 | 0.000 | 0.707 | 0.024 | 0.059 |
| ET-CYCC6 | 1.25E-11         | 0.830                                 | 0.170 | 0.000 | 2.099 | 0.183 | 0.304 | 0.745 | 0.000 | 0.847 | 0.046 | 0.175 |
| 3-ME-C6  | 7.45E-12         | 0.874                                 | 0.125 | 0.002 | 0.968 | 0.003 | 0.193 | 0.315 | 0.000 | 1.197 | 0.000 | 0.000 |
| 4-ME-C7  | 8.96E-12         | 0.840                                 | 0.157 | 0.002 | 0.933 | 0.002 | 0.002 | 0.341 | 0.000 | 1.426 | 0.000 | 0.000 |
| 4-ET-C7  | 1.09E-11         | 0.826                                 | 0.172 | 0.002 | 0.960 | 0.004 | 0.081 | 0.274 | 0.000 | 1.427 | 0.000 | 0.000 |
| 4-PR-C7  | 1.24E-11         | 0.809                                 | 0.189 | 0.002 | 0.955 | 0.002 | 0.010 | 0.322 | 0.000 | 1.430 | 0.000 | 0.000 |

(continued)

Table 6 (continued) - 6

| Name    | kOH <sup>a</sup> | Product Yield Parameters <sup>b</sup> |       |       |       |       |       | C2    |       |       |       |       |
|---------|------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|         |                  | RR                                    | NR    | XN    | R2    | A1    | A2    | A3    | K3    | K4    | CO    |       |
| BR-C6   | 5.68E-12         | 0.906                                 | 0.087 | 0.007 | 0.944 | 0.011 | 0.079 | 0.661 | 0.384 | 0.537 | 0.000 | 0.000 |
| BR-C7   | 7.45E-12         | 0.874                                 | 0.125 | 0.002 | 0.968 | 0.003 | 0.193 | 0.315 | 0.000 | 1.197 | 0.000 | 0.000 |
| BR-C8   | 8.96E-12         | 0.840                                 | 0.157 | 0.002 | 0.933 | 0.002 | 0.002 | 0.341 | 0.000 | 1.426 | 0.000 | 0.000 |
| BR-C9   | 1.09E-11         | 0.826                                 | 0.172 | 0.002 | 0.960 | 0.004 | 0.081 | 0.274 | 0.000 | 1.427 | 0.000 | 0.000 |
| BR-C10  | 1.24E-11         | 0.809                                 | 0.189 | 0.002 | 0.955 | 0.002 | 0.010 | 0.322 | 0.000 | 1.430 | 0.000 | 0.000 |
| BR-C11  | 1.44E-11         | 0.843                                 | 0.157 | 0.000 | 1.520 | 0.036 | 0.145 | 0.144 | 0.000 | 2.038 | 0.000 | 0.000 |
| BR-C12  | 1.59E-11         | 0.830                                 | 0.170 | 0.000 | 1.426 | 0.004 | 0.398 | 0.016 | 0.000 | 1.838 | 0.000 | 0.000 |
| BR-C13  | 1.74E-11         | 0.818                                 | 0.182 | 0.000 | 1.408 | 0.003 | 0.048 | 0.172 | 0.000 | 2.004 | 0.000 | 0.000 |
| BR-C14  | 1.89E-11         | 0.812                                 | 0.188 | 0.000 | 1.230 | 0.003 | 0.012 | 0.010 | 0.000 | 2.016 | 0.000 | 0.000 |
| BR-C15  | 2.04E-11         | 0.805                                 | 0.195 | 0.000 | 1.232 | 0.002 | 0.011 | 0.005 | 0.000 | 2.017 | 0.000 | 0.000 |
| CYC-C6  | 9.06E-12         | 0.865                                 | 0.135 | 0.000 | 1.313 | 0.031 | 0.000 | 1.223 | 0.000 | 0.365 | 0.015 | 0.017 |
| CYC-C7  | 1.06E-11         | 0.854                                 | 0.146 | 0.000 | 1.678 | 0.145 | 0.006 | 0.971 | 0.000 | 0.707 | 0.024 | 0.059 |
| CYC-C8  | 1.25E-11         | 0.830                                 | 0.170 | 0.000 | 2.099 | 0.183 | 0.304 | 0.745 | 0.000 | 0.847 | 0.046 | 0.175 |
| CYC-C9  | 1.41E-11         | 0.844                                 | 0.156 | 0.000 | 2.416 | 0.278 | 0.259 | 0.737 | 0.000 | 1.083 | 0.002 | 0.257 |
| CYC-C10 | 1.60E-11         | 0.834                                 | 0.166 | 0.000 | 2.208 | 0.194 | 0.385 | 0.393 | 0.000 | 1.493 | 0.030 | 0.194 |
| CYC-C11 | 1.75E-11         | 0.852                                 | 0.148 | 0.000 | 2.365 | 0.294 | 0.459 | 0.392 | 0.000 | 1.653 | 0.005 | 0.171 |
| CYC-C12 | 1.95E-11         | 0.845                                 | 0.155 | 0.000 | 2.330 | 0.264 | 0.522 | 0.243 | 0.000 | 1.810 | 0.003 | 0.165 |
| CYC-C13 | 2.10E-11         | 0.830                                 | 0.170 | 0.000 | 2.172 | 0.173 | 0.347 | 0.464 | 0.000 | 1.804 | 0.004 | 0.076 |
| CYC-C14 | 2.25E-11         | 0.821                                 | 0.178 | 0.001 | 2.123 | 0.122 | 0.154 | 0.678 | 0.000 | 1.818 | 0.006 | 0.063 |
| CYC-C15 | 2.40E-11         | 0.818                                 | 0.180 | 0.002 | 2.013 | 0.060 | 0.046 | 0.541 | 0.000 | 2.092 | 0.004 | 0.044 |
| C4C5    | 3.49E-12         | 0.950                                 | 0.048 | 0.002 | 0.804 | 0.185 | 0.571 | 0.248 | 0.347 | 0.272 | 0.000 | 0.000 |
| C6PLUS  | 6.51E-12         | 0.872                                 | 0.122 | 0.006 | 1.009 | 0.050 | 0.091 | 0.300 | 0.407 | 0.891 | 0.000 | 0.000 |

<sup>a</sup>OH radical rate constant given in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ .<sup>b</sup>Symbols for product yield parameters correspond to the notation used in Table 4.<sup>c</sup>Rate constants for reaction of OH radicals with methane were calculated using the expression  $k\text{OH} = 6.255 \times 10^{-13} \times (T/300)^2 \times \exp(-2.544/RT)$ , as recommended by Atkinson (1986, 1988). Formation of  $\text{methane} + \text{HO}_2$  following one NO to  $\text{NO}_2$  conversion is assumed to dominate.<sup>d</sup>Rate constants for reactions of OH radicals with ethane were calculated using the expression  $k\text{OH} = 1.233 \times 10^{-12} \times (T/300)^2 \times \exp(-0.882/RT)$ , as recommended by Atkinson (1986, 1988). Formation of  $\text{ethane} + \text{HO}_2$  following one NO to  $\text{NO}_2$  conversion is assumed to dominate.<sup>e</sup>The rate constants, product yields, and NO to  $\text{NO}_2$  conversions for the  $\text{C}_3+$  alkanes were derived using a computer program as follows:

(continued)

Table 6 (continued) - 7

- (1) Using the estimation techniques developed by Atkinson (1986), as recently updated (Atkinson, 1988), the rates of OH radical reaction at various positions in the alkane were calculated. These were then used to derive both the total OH radical rate constant for the alkane, and the relative yields of the various initially formed radicals.
  - (2) For each initially formed radical, the distribution of products ultimately formed in the presence of  $\text{NO}_x$ , and the total amount of NO to  $\text{NO}_2$  conversions and NO and radical consumption due to organic nitrate formation were calculated. These calculations used the alkoxy and alkyl peroxy radical branching ratio estimates given by Carter and Atkinson (1985), as updated by Atkinson (1988). The only exception to this was the decomposition rate constant assumed for the 2-butoxy radicals; in that case, the experimentally derived value (see Atkinson, 1988, and references therein) was used.
  - (3) The yields of product species in the mechanism were derived based on the distribution of individual products calculated to be formed, as follows: Formaldehyde ( $\text{HCHO}$ ), acetaldehyde ( $\text{CCHO}$ ), acetone ( $\text{ACET}$ ) and CO were represented explicitly; propionaldehyde ( $\text{RCHO}$ ) represented the higher aldehydes; methyl ethyl ketone (MEK) is used to represent the higher ketones; the lumped alkyl nitrate species ( $\text{RNO}_3$ ) was used to represent  $\text{C}_4+$  nitrates; and "Lost Nitrogen" ( $\text{-N}$ ) was used to represent  $\text{C}_3-$  nitrates, whose reactions are ignored in this mechanism. The bi- and polyfunctional products formed following alkoxy radical isomerization of the long chain alkanes were represented by RCHO and MEK. RCHO represented all the -CHO groups in these species, while MEK represented the -OH or -CO- groups. If the use of MEK to represent all the -OH and -CO- groups in these species resulted in more carbons being represented than were present in the bifunctional products, then the yield of MEK was reduced so that the resulting mixture of RCHO and MEK had the same number of carbons as the bi- and polyfunctional products.  
 (Note: A few cycloalkanes were calculated to form small yields of acyl peroxy radicals, and this could not be handled properly by this computer program. Instead, these radicals were assumed to all react with NO to form  $\text{CO}_2$  and the corresponding alkoxy radical. This is clearly an approximation, but for all acyclic alkanes and most cycloalkanes acyl peroxy radical formation is not predicted to be important. The  $\text{CO}_2$  yields tabulated for the alkanes in Table 6 indicate the extent that such radicals are predicted to be formed, since this is the only source of  $\text{CO}_2$  in these estimates of the alkane mechanism.)  
 (A computer program had to be used to carry out these derivations because of the large number of individual radical and product species predicted to be involved in the atmospheric photooxidations of the higher alkanes.)
- $\text{fC}_4\text{C}_5$  and  $\text{C}_6\text{PLUS}$  are the lumped alkane species used in the mechanism of Lurmann et al. (1987a). They are included among the detailed model species for compatibility with that mechanism, and for model simulations of UNC auto exhaust chamber runs, where these species are used to represent the alkanes present there (Carter et al. 1986). The parameters for  $\text{C}_4\text{C}_5$  were calculated by averaging those of N-C5, N-C5, ISO-C4, and ISO-C5. The parameters for C6PLUS were calculated by averaging those of N-C6, N-C7, N-C8, 23-DMB, 2-ME-C5, 23-DM-C5, and ISO-8.

Table 7. Listing of Kinetic and Mechanistic Parameters Assigned for the Aromatic Detailed Model Species

| Name   | Rate Parameters <sup>a</sup> |        | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|--|------------------------------|--------|-------------------------------------|-------|------|-------|------|-------|
|  | A                            | Ea     | Type                                | Value | Type | Value | Type | Value |
| BENZENE  | 2.50E-12                     | 0.397  | GL                                  | 0.207 | PH   | 0.270 | U1   | 0.480 |
|  |                              |        | RH                                  | 0.270 | RR   | 0.730 |      |       |
| Rate constant based on data of Wallington et al. (1987), Witte et al. (1986), and data summarized by Atkinson (1986). Phenol yields based on the data of Pitts et al. (1983) as discussed by Carter et al. (1986). Glyoxal yield based on data of Tuazon et al. (1986), as given by Atkinson (1988). Aromatic fragmentation product yield adjusted to fit O <sub>3</sub> , NO and NO <sub>2</sub> data in benzene-NO <sub>x</sub> -air runs ITC-560, 561, and 562.   |                              |        |                                     |       |      |       |      |       |
| TOLUENE  | 2.10E-12                     | -0.640 | BZ                                  | 0.080 | CR   | 0.240 | GL   | 0.118 |
|  |                              |        | MG                                  | 0.131 | U2   | 0.380 | RH   | 0.240 |
|  |                              |        | RR                                  | 0.760 |      |       |      |       |
| Rate constant recommended by Atkinson (1986) for T <= 325 K. Benzaldehyde yields based on the data of Atkinson et al. (1983) Alpha dicarbonyl yields averages of those of Bandow et al. (1985), Tuazon et al. (1986) and Gery et al. (1985) as summarized by Atkinson (1988). Cresol yields indicated by the data of Gery et al. (1985) are assumed. [The data of Atkinson et al. (1983) and Leone et al. (1985) indicate much lower yields of around 0.18, but assuming the higher yields of Gery et al. (1985) result in much better fits of model simulations to maximum ozone yields observed in SAPRC toluene-NO <sub>x</sub> -air runs.] Fragmentation product yields adjusted to fit the O <sub>3</sub> , NO, NO <sub>2</sub> , and PAN data of toluene-NO <sub>x</sub> runs EC-266, EC-270, EC-271, and ITC-699. |                              |        |                                     |       |      |       |      |       |
| C2-BENZ  | 7.50E-12                     | 0.000  | BZ                                  | 0.080 | CR   | 0.240 | GL   | 0.118 |
|  |                              |        | MG                                  | 0.131 | U2   | 0.380 | RH   | 0.240 |
|  |                              |        | RR                                  | 0.760 |      |       |      |       |
| This is ethyl benzene. Rate constant average of room temperature values tabulated by Atkinson (1986). Mechanistic parameters of toluene used for all mono-alkyl benzenes.  |                              |        |                                     |       |      |       |      |       |
| I-C3-BEN   | 6.55E-12                     | 0.000  | BZ                                  | 0.080 | CR   | 0.240 | GL   | 0.118 |
|  |                              |        | MG                                  | 0.131 | U2   | 0.380 | RH   | 0.240 |
|  |                              |        | RR                                  | 0.760 |      |       |      |       |

(continued)

Table 7 (continued) - 2

| Name   | Rate Parameters <sup>a</sup> |        | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|--|------------------------------|--------|-------------------------------------|-------|------|-------|------|-------|
|  | A                            | Ea     | Type                                | Value | Type | Value | Type | Value |
| This is isopropyl benzene. Rate constant average of room temperature values tabulated by Atkinson (1986). Mechanistic parameters of toluene used for all mono-alkyl benzenes.  |                              |        |                                     |       |      |       |      |       |
| N-C3-BEN   | 5.70E-12                     | 0.000  | BZ                                  | 0.080 | CR   | 0.240 | GL   | 0.118 |
|  |                              |        | MG                                  | 0.131 | U2   | 0.380 | RH   | 0.240 |
|  |                              |        | RR                                  | 0.760 |      |       |      |       |
| This is n-propyl benzene. Rate constant recommended by Atkinson (1986) for 298-305 K. Mechanistic parameters of toluene used for all mono-alkyl benzenes.  |                              |        |                                     |       |      |       |      |       |
| S-C4-BEN   | 5.70E-12                     | 0.000  | BZ                                  | 0.080 | CR   | 0.240 | GL   | 0.118 |
|  |                              |        | MG                                  | 0.131 | U2   | 0.380 | RH   | 0.240 |
|  |                              |        | RR                                  | 0.760 |      |       |      |       |
| This is s-butyl benzene. Assumed to have the same rate constant as n-propyl benzene. Mechanistic parameters of toluene used for all mono-alkyl benzenes.   |                              |        |                                     |       |      |       |      |       |
| M-XYLENE   | 1.66E-11                     | -0.231 | BZ                                  | 0.040 | CR   | 0.180 | RH   | 0.180 |
|  |                              |        | GL                                  | 0.108 | MG   | 0.370 | U2   | 0.620 |
|  |                              |        | RR                                  | 0.820 |      |       |      |       |
| Rate constant recommended by Atkinson (1986) for T <= 325 K. Aromatic aldehyde yields based on estimates of Atkinson (1986) and data of Bandow and Washida (1985a). Alpha dicarbonyl yield averages of those of Bandow and Washida (1985a) and Tuazon et al. (1986), as summarized by Atkinson (1988). "Cresol" yields based on data of Gery et al. (1987). Aromatic fragmentation product yields adjusted to fit the O <sub>3</sub> , NO, NO <sub>2</sub> , PAN, and m-xylene data in m-xylene-NO <sub>x</sub> -air runs EC-344, EC-345, and ITC-702. |                              |        |                                     |       |      |       |      |       |
| O-XYLENE   | 1.47E-11                     | 0.000  | BZ                                  | 0.040 | CR   | 0.180 | GL   | 0.108 |
|  |                              |        | MG                                  | 0.370 | U2   | 0.620 | RH   | 0.180 |
|  |                              |        | RR                                  | 0.820 |      |       |      |       |
| The rate constant based on the recommendation of Atkinson for 298 <= T <= 320 K. The mechanistic parameters derived for m-xylene were used for all the xylenes and dialkyl benzenes, since there are insufficient chamber data to use to derive yields of uncharacterized fragmentation products for the others.   |                              |        |                                     |       |      |       |      |       |

(continued)

Table 7 (continued) - 3

| Name   | Rate Parameters <sup>a</sup> |        | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|--|------------------------------|--------|-------------------------------------|-------|------|-------|------|-------|
|  | A                            | Ea     | Type                                | Value | Type | Value | Type | Value |
| P-XYLENE   | 1.52E-11                     | 0.000  | BZ                                  | 0.040 | CR   | 0.180 | GL   | 0.108 |
|  |                              |        | MG                                  | 0.370 | U2   | 0.620 | RH   | 0.180 |
|  |                              |        | RR                                  | 0.820 |      |       |      |       |
| Rate constant based on the recommendation of Atkinson for 297 <= T <= 320 K. The mechanistic parameters derived for m-xylene were used for all the xylenes and dialkyl benzenes, since there are insufficient chamber data to use to derive yields of uncharacterized fragmentation products for the others.   |                              |        |                                     |       |      |       |      |       |
| 135-TMB  | 5.80E-11                     | 0.000  | BZ                                  | 0.030 | CR   | 0.180 | MG   | 0.620 |
|  |                              |        | U2                                  | 0.570 | RH   | 0.180 | RR   | 0.820 |
| This is 1,3,5-trimethylbenzene. Rate constant based on unpublished results of Atkinson and Aschmann, as summarized by Atkinson (1988). Aromatic aldehyde yield based on value derived by Atkinson (1986) from kinetics data. Phenolic product yields assumed to be the same as assumed for xylenes. Methyl glyoxal yield average of values of Bandow and Washida (1985b) and Tuazon et al. (1986), as summarized by Atkinson (1988). Aromatic fragmentation product yield adjusted to fit O <sub>3</sub> , NO, NO <sub>2</sub> , PAN, and 135-TMB yields in 135-TMB-NO <sub>x</sub> -air runs EC-901, EC-903, ITC-703, ITC-706, and ITC-709. |                              |        |                                     |       |      |       |      |       |
| 123-TMB  | 3.30E-11                     | 0.000  | BZ                                  | 0.030 | CR   | 0.180 | MG   | 0.620 |
|  |                              |        | U2                                  | 0.570 | RH   | 0.180 | RR   | 0.820 |
| Rate constant based on unpublished results of Atkinson and Aschmann, as summarized by Atkinson (1988). Mechanistic parameters for 135-TMB used for all tri- and poly-alkyl benzenes.   |                              |        |                                     |       |      |       |      |       |
| 124-TMB  | 3.30E-11                     | 0.000  | BZ                                  | 0.030 | CR   | 0.180 | MG   | 0.620 |
|  |                              |        | U2                                  | 0.570 | RH   | 0.180 | RR   | 0.820 |
| Rate constant based on unpublished results of Atkinson and Aschmann, as summarized by Atkinson (1988). Mechanistic parameters for 135-TMB used for all tri- and poly-alkyl benzenes.   |                              |        |                                     |       |      |       |      |       |
| NAPHTHAL   | 1.05E-12                     | -1.792 | PH                                  | 0.170 | NP   | 0.140 | U1   | 0.320 |
|  |                              |        | RH                                  | 0.170 | RR   | 0.690 |      |       |

(continued)

Table 7 (continued) - 4

| Name  | Rate Parameters <sup>a</sup> |       | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|---|------------------------------|-------|-------------------------------------|-------|------|-------|------|-------|
|   | A                            | Ea    | Type                                | Value | Type | Value | Type | Value |
| This is naphthalene. Rate constant recommended by Atkinson (1986) for T <= 410 K. "Phenol" and "nitrophenol" (i.e., direct radical and NO <sub>x</sub> sink) yields derived by Carter et al. (1987) based on fits to chamber data were used without further adjustment. Glyoxal yield arbitrarily set at zero. (Chamber simulations not sensitive to this parameter.) Aromatic fragmentation product yield adjusted based on fits to O <sub>3</sub> , NO, and NO <sub>2</sub> data in naphthalene-NO <sub>x</sub> -air runs ITC-751, ITC-755, ITC-756, ITC-798, and ITC-802.  |                              |       |                                     |       |      |       |      |       |
| 23-DMN  | 7.70E-11                     | 0.000 | CR                                  | 0.040 | NP   | 0.160 | MG   | 0.450 |
|   |                              |       | U1                                  | 0.810 | U2   | 0.020 | RH   | 0.040 |
|   |                              |       | RR                                  | 0.800 |      |       |      |       |
| This is 2,3-dimethylnaphthalene. It is also used to represent all other di- and polyalkyl naphthalenes. Rate constant of Atkinson and Aschmann (1986) used. "Cresol" and "nitrophenol" (i.e., direct radical and NO <sub>x</sub> sink) yields derived by Carter et al. (1987) based on fits to chamber data were used without further adjustment. Glyoxal yield arbitrarily set at zero. (Chamber simulations not sensitive to this parameter.) Glyoxal and aromatic fragmentation product yields adjusted based on fits to O <sub>3</sub> , NO, NO <sub>2</sub> , PAN, and 23-DMN data in the 23-DMN-NO <sub>x</sub> -air runs ITC-771, ITC-774, ITC-775, and ITC-806. |                              |       |                                     |       |      |       |      |       |
| ME-NAPH   | 5.20E-11                     | 0.000 | PH                                  | 0.085 | CR   | 0.020 | NP   | 0.150 |
|   |                              |       | MG                                  | 0.225 | U1   | 0.565 | U2   | 0.010 |
|   |                              |       | RH                                  | 0.105 | RR   | 0.745 |      |       |
| This is used to represent all mono-alkyl naphthalenes. Rate constant of Atkinson and Aschmann (1987) for 2-methylnaphthalene used. Mechanistic parameters used are averages of those derived for naphthalene and 2,3-dimethylnaphthalene.   |                              |       |                                     |       |      |       |      |       |
| TETRALIN  | 3.43E-11                     | 0.000 | PH                                  | 0.090 | NP   | 0.120 | RR   | 0.790 |
|   |                              |       | RH                                  | 0.090 | U1   | 0.160 |      |       |
| Rate constant based on results of Atkinson and Aschmann (1988). "Phenol" and "nitrophenol" (i.e., direct radical and NO <sub>x</sub> sink) yields derived by Carter et al. (1987) based on fits to chamber data were used without further adjustment. Glyoxal and aromatic fragmentation product yields adjusted based on fits to O <sub>3</sub> , NO, NO <sub>2</sub> , and propene tracer data in tetralin-NO <sub>x</sub> -air runs ITC-739, ITC-747, ITC-748, ITC-750, and ITC-802.   |                              |       |                                     |       |      |       |      |       |

<sup>a</sup>A is the Arrhenius activation energy in cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>.Ea is the activation energy in kcal mole<sup>-1</sup>.<sup>b</sup>The symbols used to indicate the types of aromatic mechanistic parameters are based on the nomenclature used in Tables 2 and 4.

Table 8. Listing of Kinetic and Mechanistic Parameters Assigned for Alcohols and Other Miscellaneous Detailed Model Species

| Name   | Rate Parameters <sup>a</sup> |       | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|--|------------------------------|-------|-------------------------------------|-------|------|-------|------|-------|
|  | A                            | Ea    | Type                                | Value | Type | Value | Type | Value |
| ALCOHOLS AND ETHERS  |                              |       |                                     |       |      |       |      |       |
| MEOH   | 9.10E-12                     | 1.371 | A1                                  | 1.000 | RH   | 1.000 |      |       |
| <p>This is methanol. The rate parameters are recommended by Atkinson (1988). [Note: The evaluations against the chamber data, and the mechanism condensation tests were using previous recommendations of Atkinson (1986) of <math>A = 1.34 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}</math> and <math>Ea = 1.60 \text{ kcal mole}^{-1}</math>. Although these give essentially the room temperature rate constant as the current recommendation, the previous values should be used if it is desired to exactly reproduce the results of the evaluation calculations.] The reaction of methanol with OH radicals is assumed to result exclusively in formaldehyde + HO<sub>2</sub> formation.</p> |                              |       |                                     |       |      |       |      |       |
| ETOH   | 9.30E-12                     | 0.596 | A2                                  | 1.000 | RH   | 1.000 |      |       |
| <p>This is ethanol. The rate parameters are recommended by Atkinson (1988). [Note: The mechanism condensation tests were run using the previous recommendations of Atkinson (1986) of <math>A = 5.27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}</math> and <math>Ea = 0.35 \text{ kcal mole}^{-1}</math>. The previous values should be used if it is desired to exactly reproduce the results of the condensation tests.] The reaction of methanol with OH radicals is assumed to result exclusively in acetaldehyde + HO<sub>2</sub> formation.</p>   |                              |       |                                     |       |      |       |      |       |
| ME-O-ME  | 1.04E-11                     | 0.739 | A3                                  | 1.000 | RR   | 1.000 |      |       |
| <p>This is dimethylether. Rate parameters recommended by Atkinson (1988). Assumed to react to form CH<sub>3</sub>-O-CHO (represented by RCHO) + HO<sub>2</sub> after one NO to NO<sub>2</sub> conversion.</p>  |                              |       |                                     |       |      |       |      |       |
| I-C3-OH  | 5.60E-12                     |       | K3                                  | 1.000 | RH   | 1.000 |      |       |
| <p>This is isopropyl alcohol. Rate constant recommended by Atkinson (1988). [Note: the mechanism condensation tests were carried out using the previous value of <math>6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}</math>, derived from the average of the measured room temperature values tabulated by Atkinson (1986). That value should be used if it is desired to exactly duplicate the results of those calculations.] Assumed to react primarily to form HO<sub>2</sub> + acetone.</p>   |                              |       |                                     |       |      |       |      |       |

(continued)

Table 8 (continued) - 2

| Name   | Rate Parameters <sup>a</sup> |    | Mechanistic Parameters <sup>b</sup> |                         |          |                |          |                |
|--|------------------------------|----|-------------------------------------|-------------------------|----------|----------------|----------|----------------|
|  | A                            | Ea | Type                                | Value                   | Type     | Value          | Type     | Value          |
| N-C3-OH  | 5.30E-12                     |    | A1<br>RH                            | 0.230<br>0.770          | A2<br>RR | 0.230<br>0.230 | A3       | 0.770          |
| This is n-propyl alcohol. Rate constant recommended by Atkinson (1988). Mechanism estimated based on estimation techniques of Atkinson (1987) and Carter and Atkinson (1985).  |                              |    |                                     |                         |          |                |          |                |
| N-C4-OH  | 8.30E-12                     |    | A1<br>K4<br>R2                      | 0.250<br>0.090<br>0.060 | A2<br>RH | 0.120<br>0.600 | A3<br>RR | 0.850<br>0.400 |
| This is n-butyl alcohol. Rate constant recommended by Atkinson (1988). [Note: the mechanism condensation tests were carried using the previous value of $6.38 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ , derived from the average of the measured room temperature values tabulated by Atkinson (1986). That value should be used if it is desired to exactly duplicate the results of those calculations.] Mechanism estimated based on techniques of Atkinson (1987) and Carter and Atkinson (1985). |                              |    |                                     |                         |          |                |          |                |
| I-C4-OH  | 9.53E-12                     |    | K4<br>RR                            | 0.840<br>0.120          | A2       | 0.240          | RH       | 0.840          |
| This is 2-butyl alcohol. The rate constant and mechanism is estimated based on techniques of Atkinson (1987) and Carter and Atkinson (1985).   |                              |    |                                     |                         |          |                |          |                |
| T-C4-OH  | 1.09E-12                     |    | RR                                  | 1.000                   | A1       | 1.000          | K3       | 1.000          |
| This is t-butyl alcohol. The rate constant is the experimental value given by Atkinson (1987). The mechanism is based on assuming that most of the reaction occurs via initial reaction at the methyl groups.  |                              |    |                                     |                         |          |                |          |                |
| ET-GLYCL   | 7.70E-12                     |    | A2                                  | 1.000                   | RH       | 1.000          |          |                |
| This is ethylene glycol or 1,2-ethanediol. Rate constant tabulated by Atkinson (1986) used. Reaction assumed to result in glycolaldehyde + HO <sub>2</sub> , with the former being represented by acetaldehyde.  |                              |    |                                     |                         |          |                |          |                |
| PR-GLYCL   | 1.20E-11                     |    | A3                                  | 0.314                   | K4       | 0.686          | RH       | 1.000          |

(continued)

Table 8 (continued) - 3

| Name   | Rate Parameters <sup>a</sup> |       | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|--|------------------------------|-------|-------------------------------------|-------|------|-------|------|-------|
|  | A                            | Ea    | Type                                | Value | Type | Value | Type | Value |
| This is propylene glycol or 1,2-propanediol. The reaction is estimated to occur at the 1-position 31.4% of the time, forming HO <sub>2</sub> + CH <sub>2</sub> CH(OH)CHO, and at the 2-position the rest of the time, forming HO <sub>2</sub> + CH <sub>3</sub> -CO-CH <sub>2</sub> OH. The two organic products are represented by RCHO and MEK, respectively.  |                              |       |                                     |       |      |       |      |       |
| ACETYLENES   |                              |       |                                     |       |      |       |      |       |
| ACETYLEN   | 1.70E-12                     | 0.463 | GL                                  | 0.700 | RH   | 0.300 | RR   | 0.700 |
| Rate constant recommended by Atkinson (1986). Mechanism estimated based on the data of Hatakeyama et al. (1986), who observed approximately 70% glyoxal and 40% formic acid in acetylene-NO <sub>x</sub> photooxidations. The subsequent reactions of formic acid are ignored. The formation of glyoxal is assumed to involve the rearrangement of the vibrationally excited OH - acetylene adduct to .CH <sub>2</sub> CHO radicals, which adds O <sub>2</sub> and reacts with NO to form glyoxal, NO <sub>2</sub> and HO <sub>2</sub> . The formation of formic acid is assumed to occur following stabilization of the initially formed adduct, which reacts with O <sub>2</sub> and rearranges to form formic acid + HCO radicals. The later reacts with O <sub>2</sub> to form HO <sub>2</sub> and CO. |                              |       |                                     |       |      |       |      |       |
| ME-ACTYL   | 6.06E-12                     |       | A3                                  | 1.000 | RR   | 1.000 |      |       |
| This is methyl acetylene. The mechanism is essentially arbitrary.  |                              |       |                                     |       |      |       |      |       |
| GENERIC MECHANISM SPECIES <sup>c</sup>   |                              |       |                                     |       |      |       |      |       |
| CL-ALK   |                              |       | A2                                  | 1.000 | RR   | 1.000 |      |       |
| CL-OLE   |                              |       | A2                                  | 1.000 | RR   | 1.000 |      |       |
| CL-ALK is used for haloalkanes and CL-OLE is used for haloalkenes. These mechanisms are arbitrary, but for most emissions profiles these estimated compounds contribute very little to reactivity. The rate constants appropriate for the individual compound are used.  |                              |       |                                     |       |      |       |      |       |
| ET-AMINE   |                              |       | A2                                  | 1.000 | RR   | 1.000 |      |       |
| TM-AMINE   |                              |       | A1                                  | 1.000 | RR   | 1.000 |      |       |

These are used to represent mechanisms of ethyl and trimethyl amines, respectively. The rate constants are assigned in the

(continued)

Table 8 (continued) - 4

| Name  | Rate Parameters <sup>a</sup> |    | Mechanistic Parameters <sup>b</sup> |       |      |       |      |       |
|---|------------------------------|----|-------------------------------------|-------|------|-------|------|-------|
|   | A                            | Ea | Type                                | Value | Type | Value | Type | Value |
| emissions assignment file (see Section III). The mechanisms are arbitrary and probably inappropriate.   |                              |    |                                     |       |      |       |      |       |
| HCHO-H  |                              |    | A1                                  | 1.000 | RH   | 1.000 |      |       |
| CCHO-H  |                              |    | A2                                  | 1.000 | RH   | 1.000 |      |       |
| RCHO-H  |                              |    | A3                                  | 1.000 | RH   | 1.000 |      |       |
| CCOC-H  |                              |    | K3                                  | 1.000 | RH   | 1.000 |      |       |
| MEK-H   |                              |    | K4                                  | 1.000 | RH   | 1.000 |      |       |
| These are used in mechanisms where a HO <sub>2</sub> + an organic product is formed without any NO to NO <sub>2</sub> conversions. They usually occur when OH reacts with an alcohol by abstracting at the position alpha to the -OH group. The rate constant is assigned for the specific compound being represented |                              |    |                                     |       |      |       |      |       |
| HCHO-R  |                              |    | A1                                  | 1.000 | RR   | 1.000 |      |       |
| CCHO-R  |                              |    | A2                                  | 1.000 | RR   | 1.000 |      |       |
| RCHO-R  |                              |    | A3                                  | 1.000 | RR   | 1.000 |      |       |
| CCOC-R  |                              |    | K3                                  | 1.000 | RR   | 1.000 |      |       |
| MEK-R   |                              |    | K4                                  | 1.000 | RR   | 1.000 |      |       |
| A1A3-R  |                              |    | A1                                  | 1.000 | A3   | 1.000 | RR   | 1.000 |
| A2A3-R  |                              |    | A2                                  | 1.000 | A3   | 1.000 | RR   | 1.000 |
| A1A1-R  |                              |    | A1                                  | 2.000 | RR   | 1.000 |      |       |
| These are used in mechanism where HO <sub>2</sub> + organic product(s) are formed following an NO to NO <sub>2</sub> conversion. The latter three represent formation of HCHO + RCHO, CCHO + RCHO, and 2 HCHO, respectively. The rate constant is assigned for the specific compound being represented.               |                              |    |                                     |       |      |       |      |       |

<sup>a</sup>A is the Arrhenius activation energy in cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>.  
Ea is the activation energy in kcal mole<sup>-1</sup>.

<sup>b</sup>The symbols used to represent the various types of mechanistic parameters are based on those employed in Tables 2 and 4.

<sup>c</sup>Generic mechanism species are used in conjunction with the assignment of emitted organics which are not well represented by other detailed model species. Their use is discussed in Section III.

Table 9. Listing of Kinetic and Mechanistic Parameters Assigned to the Non-Ethene Alkene Species

| Name                                | Substituent Codes <sup>a</sup> | y(RNO <sub>3</sub> ) <sup>b</sup> | Rxn.     | A        | Ea     | Kinetic Parameters <sup>c</sup>             |  |
|-------------------------------------|--------------------------------|-----------------------------------|----------|----------|--------|---|--|
|                                     |                                |                                   |          |          |        | References                                  |  |
| PROPENE                             | 1 2                            | 0.000                             | OH       | 4.85E-12 | -1.001 | Atkinson (1986, 1988)                       |  |
|                                     |                                | 03                                | 1.32E-14 | 4.182    |        | Atkinson and Carter (1984), Atkinson (1988) |  |
|                                     |                                | NO3                               | 4.85E-12 | 3.699    |        | K(298) of Atkinson (1988), A of OH reaction |  |
|                                     |                                | 0                                 | 1.18E-11 | 0.644    |        | Atkinson and Lloyd (1984)                   |  |
| 1-BUTENE                            | 1 3                            | 0.000                             | OH       | 6.53E-12 | -0.930 | Atkinson (1986, 1988)                       |  |
|                                     |                                | 03                                | 3.46E-15 | 3.403    |        | Atkinson and Carter (1984), Atkinson (1988) |  |
|                                     |                                | NO3                               | 6.53E-12 | 3.730    |        | K(298) of Atkinson (1988), A of OH reaction |  |
|                                     |                                | 0                                 | 1.25E-11 | 0.648    |        | Atkinson and Lloyd (1984)                   |  |
| T-2-BUTE<br>(trans-2-<br>Butene)    | 2 2                            | 0.000                             | OH       | 1.01E-11 | -1.091 | Atkinson (1986, 1988)                       |  |
|                                     |                                | 03                                | 9.08E-15 | 2.258    |        | Atkinson and Carter (1984), Atkinson (1988) |  |
|                                     |                                | NO3                               | 1.01E-11 | 1.927    |        | K(298) of Atkinson (1988), A of OH reaction |  |
|                                     |                                | 0                                 | 2.26E-11 | -0.020   |        | Atkinson and Lloyd (1984)                   |  |
| C-2-BUTE<br>(cis-2-<br>Butene)      | 2 2                            | 0.000                             | OH       | 1.09E-11 | -0.970 | Atkinson (1986, 1988)                       |  |
|                                     |                                | 03                                | 3.52E-15 | 1.953    |        | Atkinson and Carter (1984), Atkinson (1988) |  |
|                                     |                                | NO3                               | 1.09E-11 | 2.036    |        | K(298) of Atkinson (1988), A of OH reaction |  |
|                                     |                                | 0                                 | 1.21E-11 | -0.235   |        | Atkinson and Pitts (1977)                   |  |
| ISOBUTEN                            | 1 4                            | 0.000                             | OH       | 9.51E-12 | -1.000 | Atkinson (1986, 1988)                       |  |
|                                     |                                | 03                                | 3.55E-15 | 3.364    |        | Atkinson and Carter (1984), Atkinson (1988) |  |
|                                     |                                | NO3                               | 9.51E-12 | 2.027    |        | K(298) of Atkinson (1988), A of OH reaction |  |
|                                     |                                | 0                                 | 1.76E-11 | 0.085    |        | Atkinson and Pitts (1977)                   |  |
| 2M-1-BUT<br>(2-Methyl-<br>1-Butene) | 1 5                            | 0.000                             | OH       | 1.12E-11 | -1.000 | Atkinson (1986, 1988). Ea estimated         |  |
|                                     |                                | 03                                | 3.55E-15 | 3.364    |        | Assumed to be the same as isobutene         |  |
|                                     |                                | NO3                               | 9.51E-12 | 2.027    |        | Assumed to be the same as isobutene         |  |
|                                     |                                | 0                                 | 1.76E-11 | 0.085    |        | Assumed to be the same as isobutene         |  |

(continued)

Table 9 (continued) - 2

| Name  | Substituent Codes <sup>a</sup> | y(RN03) <sup>b</sup> | Rxn. | A        | Ea     | Kinetic Parameters <sup>c</sup>             |  |
|---|--------------------------------|----------------------|------|----------|--------|---|--|
|   |                                |                      |      |          |        | References                                  |  |
| 2M-2-BUT<br>(2-Methyl-<br>2-Butene)         | 2 4                            | 0.000                | OH   | 1.92E-11 | -0.894 | Atkinson (1986, 1988)                       |  |
|   |                                |                      | O3   | 6.17E-15 | 1.586  | Atkinson and Carter (1984), Atkinson (1988) |  |
|   |                                |                      | N03  | 1.92E-11 | 0.429  | K(298) of Atkinson (1988), A of OH reaction |  |
|   |                                |                      | O    | 2.50E-11 | -0.380 | Atkinson and Pitts (1978)                   |  |
| 3M-1-BUT<br>(3-Methyl-<br>1-Butene)         | 1 3                            | 0.000                | OH   | 5.32E-12 | -1.059 | Atkinson (1986, 1988)                       |  |
|   |                                |                      | O3   | 3.46E-15 | 3.403  | Assumed to be the same as 1-butene          |  |
|   |                                |                      | N03  | 6.53E-12 | 3.730  | Assumed to be the same as 1-butene          |  |
|   |                                |                      | O    | 1.25E-11 | 0.648  | Assumed to be the same as 1-butene          |  |
| 23M2-BUT<br>(2,3-<br>Dimethyl-<br>2-Butene) | 4 4                            | 0.000                | OH   | 2.03E-11 | -1.000 | Atkinson (1986, 1988). Ea estimated.        |  |
|   |                                |                      | O3   | 3.71E-15 | 0.690  | Atkinson and Carter (1984), Atkinson (1988) |  |
|   |                                |                      | N03  | 2.03E-11 | -0.611 | K(298) of Atkinson (1988), A of OH reaction |  |
|   |                                |                      | O    | 5.58E-12 | -1.570 | Singleton et al (1975)                      |  |
| 1-PENTENE                                   | 1 3                            | 0.100                | OH   | 6.53E-12 | -0.930 | Assumed to be the same as 1-butene.         |  |
|   |                                |                      | O3   | 3.46E-15 | 3.422  | Nitrate yield estimated                     |  |
|   |                                |                      | N03  | 6.53E-12 | 3.730  | K(298) of Atkinson and Carter (1984), A of  |  |
|   |                                |                      | O    | 1.25E-11 | 0.648  | 1-butene                                    |  |
| 1-HEXENE                                    | 1 3                            | 0.225                | OH   | 6.84E-12 | -1.000 | Assumed to be the same as 1-butene          |  |
|   |                                |                      | O3   | 3.46E-15 | 3.369  | Assumed to be the same as 1-butene          |  |
|   |                                |                      | N03  | 6.53E-12 | 3.730  | Assumed to be the same as 1-butene          |  |
|   |                                |                      | O    | 1.25E-11 | 0.648  | Assumed to be the same as 1-butene          |  |

(continued)

Table 9 (continued) - 3

| Name                        | Substituent Codes <sup>a</sup> | y(RNO3) <sup>b</sup> | Rxn.     | A                    | Ea              | Kinetic Parameters <sup>c</sup>   |            |
|-----------------------------|--------------------------------|----------------------|----------|----------------------|-----------------|---|------------|
|                             |                                |                      |          |                      |                 | References  | References |
| CYC-HEXE<br>(Cyclohexene)   | 3 0                            | 0.000                | OH<br>03 | 1.25E-11<br>3.52E-15 | -1.000<br>1.944 | Atkinson (1986, 1988)<br>K(298) average of data in Atkinson (1988),<br>A of <u>cis</u> -2-butene.   |            |
|                             |                                |                      | NO3<br>0 | 1.09E-11<br>1.21E-11 | 2.036<br>-0.354 | Assumed to be same as <u>cis</u> -2-butene<br>K(298) from Atkinson (1986), and references<br>therein. A assumed to be same as<br><u>cis</u> -2-butene |            |
| CYC-PNTE<br>(Cyclopentene)  | 3 0                            | 0.000                | OH<br>03 | 1.24E-11<br>3.52E-15 | -1.000<br>1.510 | Atkinson (1986, 1988). Ea estimated.<br>K(298) low range of data in Atkinson (1988),<br>A of <u>cis</u> -2-butene                                     |            |
|                             |                                |                      | NO3<br>0 | 1.09E-11<br>1.21E-11 | 2.036<br>-0.406 | Assumed to be same as <u>cis</u> -2-butene<br>K(298) from Atkinson (1986), and references<br>therein. A assumed to be same as<br><u>cis</u> -2-butene |            |
| 13-BUTDE<br>(1,3-Butadiene) | 1 3                            | 0.000                | OH<br>03 | 1.39E-11<br>2.60E-14 | -0.930<br>4.829 | Atkinson (1986, 1988)<br>Atkinson and Carter (1984), Atkinson (1988)  |            |
|                             |                                |                      | NO3<br>0 | 1.39E-11<br>2.10E-11 | 2.934           | K(298) of Atkinson (1988), A of OH reaction<br>Atkinson (1986), and references therein.   |            |
| ISOPRENE                    | 1 3                            | 0.000                | OH<br>03 | 2.55E-11<br>1.23E-14 | -0.813<br>4.000 | Atkinson (1986, 1988)<br>Atkinson and Carter (1984), Atkinson (1988)  |            |
|                             |                                |                      | NO3<br>0 | 2.55E-11<br>6.00E-11 | 1.871           | K(298) of Atkinson (1988), A of OH reaction<br>Estimated using correlation with kOH<br>(Atkinson 1986)  |            |
| A-PINENE                    | 3 0                            | 0.380                | OH       | 1.20E-11             | -0.882          | Atkinson (1986, 1988). Nitrate yield<br>estimated <sup>d</sup>  |            |
|                             |                                |                      | NO3<br>0 | 9.60E-16<br>1.20E-11 | 1.453<br>0.431  | Atkinson (1988)<br>K(298) of Atkinson (1988), A of OH reaction<br>Atkinson (1986) and references therein.   |            |

(continued)

Table 9 (continued) - 4

| Name     | Substituent Codes <sup>a</sup> | y(RNO3) <sup>b</sup> | Rxn. | A        | Ea     | Kinetic Parameters <sup>c</sup><br>References   |
|----------|--------------------------------|----------------------|------|----------|--------|---|
| B-PINENE | 1 3                            | 0.380                | OH   | 2.36E-11 | -0.709 | Atkinson (1986, 1988). Nitrate yield estimated<br>K(298) of Atkinson (1988), A of isobutene<br>K(298) of Atkinson (1988), A of OH reaction<br>Atkinson (1986) and references therein. |

The following are used for unspeciated terminal alkenes. Kinetic parameters of 1-Hexene used.  
Nitrate yields estimated.<sup>d</sup>

|          |   |   |       |
|----------|---|---|-------|
| C6-OLE1  | 1 | 3 | 0.225 |
| C7-OLE1  | 1 | 3 | 0.270 |
| C8-OLE1  | 1 | 3 | 0.330 |
| C9-OLE1  | 1 | 3 | 0.360 |
| C10-OLE1 | 1 | 3 | 0.380 |
| C11-OLE1 | 1 | 3 | 0.395 |
| C12-OLE1 | 1 | 3 | 0.400 |
| C13-OLE1 | 1 | 3 | 0.410 |
| C14-OLE1 | 1 | 3 | 0.412 |
| C15-OLE1 | 1 | 3 | 0.415 |

The following are used for unspeciated internal alkenes. Kinetic parameters of trans-2-butene used.  
Nitrate yields estimated.<sup>d</sup>

|          |   |   |       |
|----------|---|---|-------|
| C5-OLE2  | 2 | 3 | 0.100 |
| C6-OLE2  | 3 | 3 | 0.225 |
| C7-OLE2  | 3 | 3 | 0.270 |
| C8-OLE2  | 3 | 3 | 0.330 |
| C9-OLE2  | 3 | 3 | 0.360 |
| C10-OLE2 | 3 | 3 | 0.380 |
| C11-OLE2 | 3 | 3 | 0.395 |
| C12-OLE2 | 3 | 3 | 0.400 |
| C13-OLE2 | 3 | 3 | 0.410 |
| C14-OLE2 | 3 | 3 | 0.412 |
| C15-OLE2 | 3 | 3 | 0.415 |

(continued)

Table 9 (continued) - 5

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<sup>a</sup>Substituent codes are as follows: 1) =CH<sub>2</sub>; 2) =CHCH<sub>3</sub>; 3) =CHR; 4) =C(CH<sub>3</sub>)<sub>2</sub>; 4) =C(CH<sub>3</sub>)(R)

or =C(R)<sup>2</sup>, where R not H or CH<sub>3</sub>.

<sup>b</sup>Nitrate yield in OH reaction  
c"R<sub>xn</sub>" = species reacting with alkene; "A" = Arrhenius A factor in cm<sup>3</sup> molecule<sup>-2</sup> sec<sup>-1</sup>; "E<sub>a</sub>" = activation energy in kcal mole<sup>-1</sup>.

<sup>d</sup>Nitrate yields estimated based on yields from alkanes with same number of carbons. Based on nitrate yields derived from results of model simulations of 1-hexene-NO<sub>x</sub>-air chamber runs (Carter et al. 1987).

B. Evaluation Against Results of Environmental Chamber Runs

The updated detailed mechanism was tested by comparing its predictions against the results of the set of over 500 environmental chamber runs which were used to test the previous version of the mechanism. These consist of experiments carried out in the SAPRC 5800-liter evacuable chamber (EC), the SAPRC 6000-liter indoor Teflon chamber (ITC), the SAPRC 50,000-liter dual outdoor Teflon chamber (ITC), and the University of North Carolina (UNC)'s 150,000-liter dual outdoor chambers. The major characteristics of these chambers, and the types of runs which were carried out in each, are discussed elsewhere (see Carter et al. 1986 and references therein), and that discussion is not duplicated here. The runs that were simulated included those which were used in the evaluation summarized by Lurmann et al. (1987a), which consists of the runs simulated in our previous study (Carter et al. 1987), combined with runs employing single compounds or known mixtures which were carried out subsequently in our Air Force program (Carter et al. 1987), but excluding the UNC "dynamic" runs which were included in the earlier study. (The "dynamic" runs were not simulated because they require special procedures for preparing the mechanism when used with our chamber modeling software. The earlier study showed that the performance of the mechanism in simulating these runs was comparable to simulations of static runs, and thus including these runs in our model evaluation set was not judged to be worth the extra effort required to simulate them.) The results of the simulations of these experiments are summarized in this section.

The procedures used to test our mechanisms against environmental chamber runs have been documented by us in detail previously (Carter et al. 1986), and that discussion is not duplicated here. Briefly, evaluating photochemical mechanisms requires provisions for representing chamber dependent processes such as the intensity and spectral characteristics of the light source, ozone wall loss and other heterogeneous processes, chamber-dependent radical sources, contaminant offgassing, and dilution. The representation of these effects used in this evaluation are the same as described by Carter et al. (1986), with the exception of the radical input rates used in simulating the SAPRC ITC runs, where the somewhat modified values discussed in Table 17 of Carter et al. (1987) were employed. As with the previous studies, no run-to-run adjustment of

chamber dependent parameters was carried out in order to optimize the fits of the model to the chamber results.

The performance of the mechanism in simulating the results of the chamber runs was measured using several criteria. These are: (1) ability to simulate maximum ozone yields; (2) ability to simulate rates of ozone formation and NO oxidation; (3) ability to simulate half lives of selected relatively rapidly reacting reactants; and (4) ability to simulate yields of formaldehyde and PAN. The methods for determining these quantities are reasonably obvious except the rates of ozone formation and NO oxidation, which can be measured in a number of ways. The measure used in this study is that employed by us previously (Carter et al. 1987, Lurmann et al. 1987a), and is one-half the maximum change in the quantity ( $[O_3] - [NO]$ ), divided by the time required to achieve this change. Thus this quantity is a measure of the average rate of NO oxidation and ozone formation during the time when NO oxidation and/or ozone formation is generally occurring most rapidly.

The fully detailed mechanism was not used in the simulations of runs containing complex mixtures of many organics. In these cases, the detailed mechanism was still used for the reactions of the inorganic species and the major photooxidation products, but lumping techniques were used to represent the reactions of complex mixtures of alkanes, aromatics, and the alkenes other than ethene. Seven lumped groups were used to represent the reactions of the alkanes and aromatics, ethene was represented explicitly, and three were used to represent the reactions of the other alkenes. The rate constant for reaction with OH radicals was used to determine which species were lumped with which. For each group, the kinetic and mechanistic parameters used for the lumped groups were determined based on the specific mixture of compounds being represented, using software which is discussed in detail elsewhere (Carter 1987). The rate constants used to determine the seven lumped alkane/aromatic groups for the detailed model evaluation were (in units of  $10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ ) 0.5, 0.75, 1.0, 1.5, 2.0, and 4.0, and the rate constants used to determine the three higher alkene lumped groups were (in the same units) 6.0 and 8.0. (In the case of the alkenes, this results in propene, 1-butene, and similar 1-alkenes being lumped into one group, isopropene and other iso-alkenes being lumped into another, and the internal alkenes being lumped into the third group.)

Test calculations, discussed in Section IV, below, showed that this representation of lumped alkanes, aromatics, and alkenes is sufficiently detailed that the results would not be significantly different if explicit representation of all species were employed. Thus, the results of this evaluation can be considered to reflect the performance of the fully detailed mechanism.

A summary of the performance of the model in simulating the maximum ozone, the average NO oxidation/ozone formation rate, and the maximum PAN yield is given in Table 10. A complete tabulation of the performance of this mechanism in simulating these quantities, and also selected reactant half lives and (where data are available) maximum formaldehyde yields, are given in the tables in Appendix A. The summary data in Table 10 can be compared with the performance of the previous version of the mechanism reported by Carter et al. (1987), which is given in Table 11.

It can be seen from comparing the data in Tables 10 and 11, and also by comparing the detailed tabulations in Appendix A with the corresponding tabulations given by Lurmann et al. (1987a), that the performance of the current mechanism is comparable to the performance of the previous version. Some runs were simulated somewhat better, and some were simulated somewhat worse, but, in general, it can be concluded that there is no significant improvement or deterioration in the ability of the model to simulate these data. This reflects, to a large extent, the fact that cases of poor performance of the model in simulating results of individual runs are probably due primarily to uncertainties in characterization of chamber effects (Carter et al. 1986). For example, the poor performance of both mechanisms in simulating results of alkane runs is due to the extreme sensitivity of these runs to chamber radical sources, which tend to vary from run-to-run. As indicated above, there was no change in the way chamber effects are represented in this evaluation compared to that reported for the previous version (Carter et al. 1987; Lurmann et al. 1987a). In addition, there was relatively little change in the representation of the most uncertain aspects of the mechanism, such as the reactions of the aromatics, the ozone alkene reactions, etc. Thus, the detailed discussion given by Carter et al. (1986) concerning the performance of the mechanism in simulating the various types of runs is still largely applicable to this updated mechanism.

Table 10. Averages of Percentage Biases<sup>a</sup> and Errors<sup>b</sup> in Model Simulations of Maximum Ozone, Average NO Oxidation and Ozone Formation Rates, and Maximum PAN Yields for All Runs Simulated Using the Current Updated Detailed Mechanism<sup>c</sup>

| Run Type                                 | No. Runs | Maximum Ozone |      | Avg. $d/dt ([O_3]-[NO])$ <sup>d</sup> |      | Maximum PAN |      |
|--|----------|---------------|------|---------------------------------------|------|-------------|------|
|  |          | Bias          | Err. | Bias                                  | Err. | Bias        | Err. |
| Formaldehyde                             | 15       | -1            | 29   | 32                                    | 33   |             |      |
| Acetaldehyde                             | 5        | -15           | 16   | -3                                    | 7    | -4          | 29   |
| Other carbonyls                          | 5        | 20            | 39   | 11                                    | 13   | 169         | 169  |
| Ethene                                   | 14       | 5             | 20   | 3                                     | 20   |             |      |
| Propene                                  | 49       | 9             | 17   | 12                                    | 18   | 24          | 37   |
| 1-Butene                                 | 11       | 39            | 50   | 38                                    | 46   | -7          | 35   |
| 1-Hexene                                 | 4        | 16            | 16   | 21                                    | 21   |             |      |
| <i>trans</i> -2-Butene                   | 3        | -10           | 17   | -6                                    | 26   | -28         | 39   |
| Isobutene                                | 1        | 8             | 8    | 5                                     | 5    | -76         | 76   |
| n-Butane                                 | 27       | 43            | 75   | 36                                    | 43   | 38          | 94   |
| Branched alkanes                         | 7        | 56            | 56   | 27                                    | 27   | -76         | 76   |
| C <sub>5</sub> -C <sub>9</sub> n-Alkanes | 13       | 74            | 91   | 5                                     | 30   |             |      |
| Methyl cyclohexane                       | 4        | e             |      | 39                                    | 39   |             |      |
| Benzene                                  | 6        | 17            | 17   | 18                                    | 19   |             |      |
| Toluene                                  | 20       | 13            | 22   | 9                                     | 18   | 10          | 37   |
| Xylenes                                  | 10       | -2            | 14   | 15                                    | 22   | -12         | 20   |
| Mesitylene                               | 8        | -1            | 24   | 17                                    | 25   | -51         | 51   |
| Tetralin                                 | 5        | -28           | 28   | -8                                    | 10   |             |      |
| Naphthalene                              | 5        | 12            | 32   | -3                                    | 8    |             |      |
| 2,3-Dimethylnaph.                        | 4        | 8             | 20   | -2                                    | 7    | -37         | 37   |
| Simple mixtures <sup>f</sup>             | 40       | 20            | 42   | 1                                     | 21   | 44          | 71   |
| Surrogate mixes <sup>g</sup>             | 146      | 14            | 24   | 14                                    | 24   | 16          | 41   |
| Auto exhaust                             | 28       | 11            | 23   | 9                                     | 17   | -11         | 31   |
| Synthetic jet fuel                       | 11       | 15            | 15   | 20                                    | 20   |             |      |
| Synthetic jet exhaust                    | 4        | -4            | 6    | -11                                   | 11   | 41          | 41   |

<sup>a</sup>Bias = average percent discrepancy. Positive number means model prediction is high. Runs with maximum ozone too low are not used for comparisons of maximum ozone.

<sup>b</sup>Error = average of absolute values of percent discrepancies.

<sup>c</sup>Excluding characterization runs.

<sup>d</sup>Average NO oxidation/ozone formation rate = one-half of the maximum change in  $([O_3]-[NO])$ , divided by the time required to achieve this change.

<sup>e</sup>None of these runs had sufficiently high maximum ozone yields for meaningful comparison.

<sup>f</sup>"Simple" mixtures = mixtures of more than one organic which do not have at least one of each of an alkane, alkene, and aromatic.

<sup>g</sup>"Surrogate" mixtures = mixtures which have at least one of each of an alkane, alkene, and aromatic.

Table 11. --Averages of Percentage Biases<sup>a</sup> and Errors<sup>b</sup> in Model Simulations of Maximum Ozone, Average NO Oxidation and Ozone Formation Rates, and Maximum PAN Yields for All Runs Simulated Using the Previous Detailed Mechanism<sup>c</sup> (from Carter et al. 1987)

| Run Type                                 | No.<br>Runs | Maximum<br>Ozone |      | Avg. d/dt<br>([O <sub>3</sub> ]-[NO]) <sup>d</sup> |      | Maximum<br>PAN |      |
|--|-------------|------------------|------|--|------|----------------|------|
|  |             | Bias             | Err. | Bias   | Err. | Bias           | Err. |
| Formaldehyde                             | 15          | -1               | 19   | 24   | 26   |                |      |
| Acetaldehyde                             | 5           | -26              | 26   | -13  | 13   | 1              | 20   |
| Other carbonyls                          | 5           | 4                | 44   | 0  | 20   | 193            | 207  |
| Ethene                                   | 14          | 12               | 23   | 6  | 22   |                |      |
| Propene                                  | 49          | 3                | 18   | 13   | 26   | 34             | 45   |
| 1-Butene                                 | 11          | 17               | 39   | 30   | 42   | -34            | 34   |
| 1-Hexene                                 | 4           | -1               | 4    | 14   | 14   |                |      |
| <u>trans</u> -2-Butene                   | 3           | -29              | 29   | 24   | 25   | -13            | 23   |
| Isobutene                                | 1           | 7                | 7    | 46   | 46   | -69            | 69   |
| n-Butane                                 | 27          | 26               | 62   | 38   | 56   | 44             | 95   |
| Branched alkanes                         | 7           | 34               | 49   | 18   | 19   | -70            | 70   |
| C <sub>5</sub> -C <sub>9</sub> n-Alkanes | 13          | 53               | 64   | 7  | 29   |                |      |
| Méthyl cyclohexane                       | 4           | e                |      | 51   | 51   |                |      |
| Benzene                                  | 6           | 4                | 5    | 19   | 22   |                |      |
| Toluene                                  | 20          | 13               | 24   | 9  | 20   | 25             | 45   |
| Xylenes                                  | 10          | -9               | 16   | 12   | 22   | -6             | 23   |
| Mesitylene                               | 8           | -11              | 21   | 15   | 16   | -42            | 45   |
| Tetralin                                 | 5           | -16              | 21   | -18  | 18   |                |      |
| Naphthalene                              | 5           | 4                | 25   | -1   | 9    |                |      |
| 2,3-Dimethylnaph.                        | 4           | -1               | 14   | 4  | 10   | -25            | 38   |
| Simple mixtures <sup>f</sup>             | 40          | 11               | 36   | -1   | 20   | 44             | 65   |
| Surrogate mixes <sup>g</sup>             | 146         | 5                | 22   | 10   | 26   | 27             | 46   |
| Auto exhaust                             | 28          | -1               | 21   | 5  | 17   | -2             | 33   |
| Synthetic jet fuel <sup>h</sup>          | 11          | 7                | 8    | 24   | 24   |                |      |
| Synthetic jet exhaust                    | 4           | -6               | 8    | -11  | 11   | 50             | 50   |

<sup>a</sup>Bias = average percent discrepancy. Positive number means model prediction is high. Runs with maximum ozone too low are not used for comparisons of maximum ozone.

<sup>b</sup>Error = average of absolute values of percent discrepancies.

<sup>c</sup>Excluding characterization runs.

<sup>d</sup>Average NO oxidation/ozone formation rate = one-half of the maximum change in ([O<sub>3</sub>]-[NO]), divided by the time required to achieve this change.

(continued)

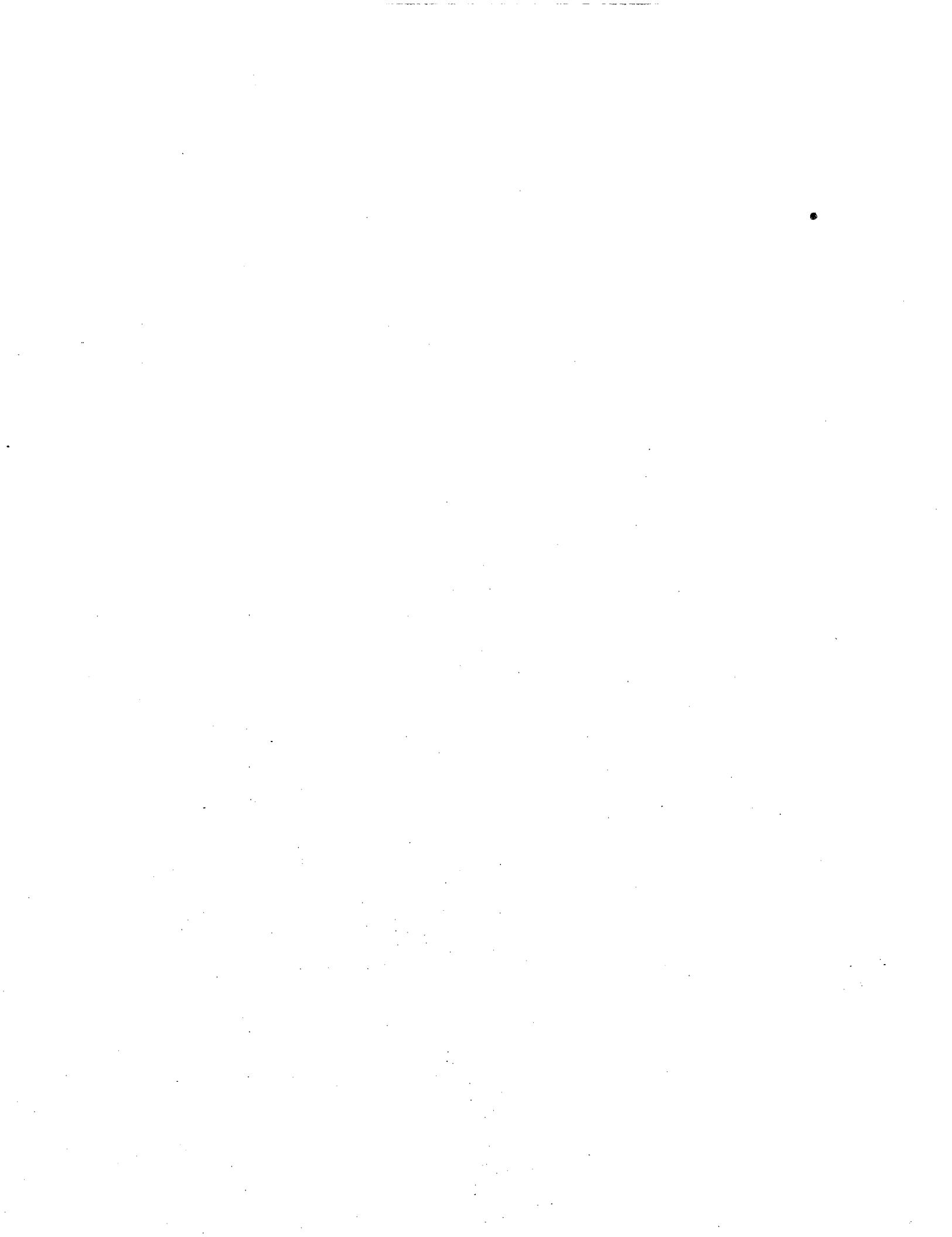
Table 11 (continued) - 2

eNone of these runs had sufficiently high maximum ozone yields for meaningful comparison.

f"Simple" mixtures = mixtures of more than one organic which do not have at least one of each of an alkane, alkene, and aromatic.

g"Surrogate" mixtures = mixtures which have at least one of each of an alkane, alkene, and aromatic.

hRuns with added furan, thiophene, and pyrrole are excluded.



### III. REPRESENTATION OF ORGANIC EMISSIONS

Current emissions inventories include many hundreds of different organic compounds, and means for representing these in the detailed and lumped mechanisms were developed as part of this program. This has involved effort in three areas: (1) developing mechanisms or assigning mechanistic and kinetic parameters to detailed model species representing the ranges of types of chemicals which are emitted; (2) determining how to represent the chemical categories used in current emissions inventories with the species in the chemical mechanism, and (3) developing software which can process emissions data for input into airshed models such that the detailed chemical information contained in emissions profiles can be incorporated into the airshed model. The results of the first effort is documented in the tabulations in the previous section, and the results of the third effort, the development of new emissions processing software, is documented in a separate report (Carter 1988). The second task, assigning the detailed species in the mechanism to the chemical categories used emissions profiles, and making the related estimates which are necessary in determining how to representing current emissions data in models using this mechanism, is documented in this section.

#### A. Detailed Model Species Used to Represent Emitted Organics

The detailed model species which were used in the assignments of the emissions profiles are listed and described in Table 12. As indicated there, there are essentially four types of detailed model species: (1) those species, such as formaldehyde and ethene, which are represented explicitly in the detailed mechanism; (2) those species, such as the many individual alkanes, aromatics, and higher alkenes which are represented in the mechanism using generalized reactions with variable kinetic and mechanistic parameters assigned for each species; (3) those species, such as the higher aldehydes and ketones, which are represented by other species in the mechanism using the "surrogate species" approach; and (4) the "generic mechanism" species, which are used to specify the mechanistic parameters for compounds in the emissions profiles which are not well represented by any of the other types of detailed model species. The mechanisms or parameters used for the species in the first two categories

Table 12. Listing of Detailed Model Species Used to Represent Individual Organics or Mixtures in Emissions Profiles

| Name(s)   | Notes <sup>a</sup> | Description  |
|---|--------------------|--|
| Species Represented Using The Generalized Alkane/Aromatic Mechanism |                    |  |
| Alkanes   |                    |  |
| METHANE   | 1                  | Methane  |
| ETHANE  | 1                  | Ethane   |
| PROPANE   | 1                  | Propane  |
| N-C4  | 1                  | n-Butane   |
| ISO-C4  | 3                  | Isobutane  |
| N-C5  | 3                  | n-Pentane  |
| ISO-C5  | 3                  | Isopentane   |
| NEO-C5  | 3                  | Neopentane   |
| CYCC5   | 3                  | Cyclopentane   |
| N-C6  | 3                  | n-Hexane   |
| 2-ME-C5   | 3                  | 2-Methylpentane  |
| 3-ME-C5   | 3                  | 3-Methylpentane  |
| 22-DMB  | 3                  | 2,2-Dimethylbutane   |
| 23-DMB  | 3                  | 2,3-Dimethylbutane   |
| CYCC6   | 3                  | Cyclohexane  |
| ME-CYCC5  | 3                  | Methylcyclopentane   |
| N-C7  | 3                  | n-Heptane  |
| 3-ME-C6   | 3                  | 3-Methylhexane   |
| 24-DM-C5  | 3                  | 2,4-Dimethylpentane  |
| 23-DM-C5  | 3                  | 3,4-Dimethylpentane  |
| ME-CYCC6  | 3                  | Methylcyclohexane  |
| N-C8  | 3                  | n-Octane   |
| 4-ME-C7   | 3                  | 4-Methylheptane  |
| ISO-C8  | 3                  | 2,2,4-Trimethylpentane   |
| ET-CYCC6  | 3                  | Ethylcyclohexane   |
| 4-ET-C7   | 3                  | 4-Ethylheptane   |
| N-C10   | 3                  | n-Decane   |
| 4-PR-C7   | 3                  | 4-Propylheptane  |
| N-C11   | 3                  | n-Undecane   |
| N-C12   | 3                  | n-Dodecane   |
| N-C13   | 3                  | n-Pentadecane  |
| N-C14   | 3                  | n-Tetradecane  |
| N-C15   | 3                  | n-Pentadecane  |
| C4C5  | 3                  | Lumped C <sub>4</sub> -C <sub>5</sub> Alkanes used in the lumped mechanism of Lurmann et al. (1987a) |
| C6PLUS  | 3                  | Lumped higher alkanes used in the lumped mechanism of Lurmann et al. (1987a)                         |
| BR-C5 - BR-C15  | 3                  | Unspeciated branched alkanes <sup>b</sup>  |
| CYC-C7 - CYC-C15  | 3                  | Unspeciated cycloalkanes <sup>b</sup>  |

(continued)

Table 12 (continued) - 2

| Name(s)                                      | Notes <sup>a</sup> | Description  |
|--|--------------------|--|
| <b>Aromatics</b>                             |                    |  |
| BENZENE                                      | 2                  | Benzene  |
| TOLUENE                                      | 2                  | Toluene  |
| C2-BENZ                                      | 2                  | Ethylbenzene   |
| M-XYLENE                                     | 3                  | m-Xylene   |
| O-XYLENE                                     | 3                  | o-Xylene   |
| P-XYLENE                                     | 3                  | p-Xylene   |
| I-C3-BEN                                     | 3                  | Isopropylbenzene   |
| N-C3-BEN                                     | 3                  | n-Propylbenzene  |
| 123-TMB                                      | 3                  | 1,2,3-Trimethylbenzene   |
| 124-TMB                                      | 3                  | 1,2,4-Trimethylbenzene   |
| 135-TMB                                      | 2                  | 1,3,5-Trimethylbenzene   |
| S-C4-BEN                                     | 3                  | s-Butylbenzene   |
| TETRALIN                                     | 2                  | Tetralin. Also used for indans                                     |
| NAPHTHAL                                     | 2                  | Naphthalene  |
| ME-NAPH                                      | 4                  | Monoalkylnaphthalenes <sup>c</sup>                                 |
| 23-DMN                                       | 2                  | 2,3-Dimethylnaphthalene (and other di- and poly-alkylnaphthalenes) |
| <b>Other Species (Lumped as Alkanes)</b>     |                    |  |
| MEOH   | 1                  | Methanol   |
| ETOH   | 1                  | Ethanol  |
| ME-O-ME                                      | 3                  | Dimethyl ether   |
| I-C3-OH                                      | 3                  | Isopropyl alcohol  |
| N-C3-OH                                      | 3                  | n-Propyl alcohol   |
| N-C4-OH                                      | 3                  | n-Butyl alcohol  |
| I-C4-OH                                      | 3                  | iso-Butyl alcohol  |
| T-C4-OH                                      | 3                  | tert-Butyl alcohol   |
| ET-GLYCL                                     | 3                  | Ethylene glycol  |
| PR-GLYCL                                     | 3                  | Propylene glycol   |
| ACETYLEN                                     | 5                  | Acetylene  |
| ME-ACTYL                                     | 5                  | Methyl acetylene   |
| ET-AMINE                                     | 5                  | Ethyl amine  |
| TM-AMINE                                     | 5                  | Trimethyl amine  |
| <b>Generic Mechanism Species<sup>d</sup></b> |                    |  |
| CL-ALK                                       | 5                  | General halogenated alkane mechanism                               |
| CL-OLE                                       | 5                  | General halogenated alkane mechanism                               |

(continued)

Table 12 (continued) - 3

| Name(s) | Notes <sup>a</sup> | Description  |
|---------|--------------------|--|
| HCHO-H  | 1                  | Species which forms HO <sub>2</sub> + HCHO   |
| CCHO-H  | 1                  | Species which forms HO <sub>2</sub> + acetaldehyde   |
| RCHO-H  | 1                  | Species which forms HO <sub>2</sub> + higher aldehyde  |
| CCOC-H  | 1                  | Species which forms HO <sub>2</sub> + acetone  |
| MEK-H   | 1                  | Species which forms HO <sub>2</sub> + higher ketones   |
| HCHO-R  | 1                  | Species which forms HO <sub>2</sub> + HCHO + 1 NO to NO <sub>2</sub> conversion  |
| CCHO-R  | 1                  | Species which forms HO <sub>2</sub> + acetaldehyde + 1 NO to NO <sub>2</sub> conversion  |
| RCHO-R  | 1                  | Species which forms HO <sub>2</sub> + higher aldehyde + 1 NO to NO <sub>2</sub> conversion   |
| CCOC-R  | 1                  | Species which forms HO <sub>2</sub> + acetone + 1 NO to NO <sub>2</sub> conversion   |
| MEK-R   | 1                  | Species which forms HO <sub>2</sub> + higher ketones + 1 NO to NO <sub>2</sub> conversion  |
| A1A1-R  | 1                  | Species which forms HO <sub>2</sub> + 2 HCHO + 1 NO to NO <sub>2</sub> conversion  |
| A1A3-R  | 1                  | Species which forms HO <sub>2</sub> + HCHO + acetaldehyde + 1 NO to NO <sub>2</sub> conversion                                       |
| A2A3-R  | 1                  | Species which forms HO <sub>2</sub> + acetaldehyde + higher ketone + 1 NO to NO <sub>2</sub> conversion                              |
| [name]  | varies             | Species which reacts to form the same products, radicals, and NO to NO <sub>2</sub> conversions as the named detailed model species. |

## Species Represented Using the Generalized Alkene Reactions

|          |   |   |
|----------|---|---|
| PROPENE  | 1 | Propene   |
| 1-BUTENE | 2 | 1-Butene  |
| C-2-BUTE | 3 | <u>cis</u> -2-Butene  |
| T-2-BUTE | 2 | <u>trans</u> -2-Butene  |
| ISOBUTEN | 2 | Isobutene   |
| 13-BUTDE | 4 | 1,3-Butadiene   |
| 1-PENTEN | 3 | 1-Pentene   |
| 2M-1-BUT | 3 | 2-Methyl-1-butene   |
| 3M-1-BUT | 3 | 2-Methyl-1-butene   |
| 2M-2-BUT | 3 | 2-Methyl-2-butene   |
| CYC-PNTE | 4 | Cyclopentene  |
| ISOPRENE | 4 | Isoprene  |
| 1-HEXENE | 2 | 1-Hexene  |
| 23M2-BUT | 3 | 2,3-Dimethyl-2-butene   |
| CYC-HEXE | 4 | Cyclohexene   |
| A-PINENE | 4 | Alpha pinene and other terpenes with only external double bonds |

(continued)

Table 12 (continued) - 4

| Name(s)   | Notes <sup>a</sup> | Description  |
|---|--------------------|--|
| B-PINENE  | 4                  | Beta pinene and other terpenes with internal double bonds  |
| C4-OLE1<br>- C15-OLE1                             | 3                  | Unspeciated terminal alkenes <sup>e</sup>                  |
| C5-OLE2<br>- C15-OLE2                             | 3                  | Unspeciated internal alkenes <sup>f</sup>                  |
| Explicitly Represented Species <sup>g</sup>       |                    |  |
| CO  | 1                  | Carbon monoxide  |
| ETHENE  | 1                  | Ethene (ETHE)  |
| FORMALD   | 1                  | Formaldehyde (HCHO)  |
| ACETALD   | 1                  | Acetaldehyde (CCHO)  |
| PROPALD   | 3                  | Propionaldehyde and all higher aldehydes (RCHO)            |
| ACETONE   | 3                  | Acetone (ACET)   |
| MEK   | 3                  | Methyl ethyl ketone and all C <sub>4</sub> + ketones (MEK) |
| GLYOXAL   | 3                  | Glyoxal (GLY)  |
| MEGLYOX   | 3                  | Methylglyoxal (MGLY)                                       |
| BENZALD   | 3                  | Benzaldehyde and other aromatic aldehydes (BALD)           |
| PHENOL  | 3                  | Phenol (PHEN)  |
| CRESOL  | 3                  | Cresols and other alkyl phenols (CRES)                     |
| RONO2   | 3                  | Alkyl nitrates (RNO <sub>3</sub> )                         |
| Unreactive Species                                |                    |  |
| INERT   | 1                  | Unreactive organics  |
| Species Represented by Other Species <sup>h</sup> |                    |  |
| N-C16 - N-C22                                     | 4                  | Higher n-alkanes (N-C15)                                   |
| CYC-C3  | 3                  | Cyclopropane (INERT)                                       |
| ET-ACTYL  | 5                  | Ethyl acetylene (1-BUTENE)                                 |
| ACROLEIN  | 4                  | Acrolein (RCHO)  |
| METHACRO  | 4                  | Methyl acrolein (RCHO)                                     |
| MVK   | 4                  | Methyl vinyl ketone (MEK)                                  |
| ALK1BENZ  | 3                  | Unspeciated monoalkyl benzenes (TOLUENE)                   |
| ALK2BENZ  | 3                  | Unspeciated dialkyl benzenes (M-XYLENE)                    |
| ALK3BENZ  | 3                  | Unspeciated trialkyl benzenes (135-TMB)                    |
| ALK4BENZ  | 4                  | Unspeciated tetraalkyl benzenes (135-TMB)                  |

(continued)

Table 12 (continued) - 5

| Name(s)  | Notes <sup>a</sup> | Description                                     |
|----------|--------------------|---|
| ALK5BENZ | 4                  | Unspeciated pentaalkyl benzenes (135-TMB)       |
| ALK1NAPH | 4                  | Unspeciated monoalkyl naphthalenes<br>(ME-NAPH) |
| DM-NAPH  | 4                  | Unspeciated dimethyl naphthalenes (23-DMN)      |
| ALK2NAPH | 4                  | Unspeciated dialkyl naphthalenes (23-DMN)       |
| ALK3NAPH | 4                  | Unspeciated trialkyl naphthalenes (23-DMN)      |

<sup>a</sup>Codes used for notes are as follows:

1. Mechanism and rate constant is either well established, or straightforward to derive based on current knowledge, or (for "pure mechanism" pseudo-species) is set by definition.
2. Mechanism uncertain in details, but derived based on fits of model simulations to environmental chamber data.
3. Mechanism estimated based on established estimation techniques of Atkinson (1986, 1987) and/or Carter and Atkinson (1985), or assumed to be similar to similar compound whose mechanism is established, or derived from chamber data.
4. Estimate of mechanistic parameters is uncertain, and needs to be evaluated.
5. Appropriate mechanistic parameters are highly uncertain.

Values used in current model are essentially arbitrary.

<sup>b</sup>Mechanism used are based on those for representative compounds of this type.<sup>c</sup>Mechanistic parameters are averages of those for naphthalene and 2,3-dimethylnaphthalene.<sup>d</sup>These are used in the emissions assignments to specify aspects of the mechanism other than the OH radical rate constant. The OH radical rate constant is specified explicitly depending on which compound is being represented. See text.<sup>e</sup>Mechanism of 1-butene used for C4-OLE1. For the higher terminal alkenes, the mechanism of 1-hexene was used, except for the nitrate yield in the OH reaction, which were estimated to be approximately the same as in n-alkanes with the same number of carbons.<sup>f</sup>Mechanism of trans-2-butene used, except for the nitrate yield in the OH reaction, which were estimated as indicated above for the terminal alkenes.<sup>g</sup>These are species which are explicitly represented in the detailed mechanism. Some of these are represented by other species in the condensed versions of the mechanism (see Section IV). If the name used for this species in the mechanism is different from the detailed model species name used in the emissions assignments, the name used in the mechanism is given in parentheses following the description.<sup>h</sup>The model species used to represent these species are indicated in parentheses following the description.

are given in the tabulations in the previous section, and the "surrogate species" representations are indicated where applicable in Table 12.

The "generic mechanism" species were used to represent species in emissions profiles which are not considered to be well represented by the other detailed model species in this mechanism. These were used in several ways: (1) For several classes of compounds, such as the haloalkanes and the haloalkenes, we have reasonably good data or estimates of their OH radical rate constants, but the details of their reaction mechanisms are highly uncertain. In those cases, we used simplified "generic mechanisms" for all species of a given type (e.g., "CL-ALK" for the haloalkanes and "CL-OLE" for the haloalkenes), but with the OH radical rate constant assigned for each individual compound. (2) For other classes of compounds, for which we could make mechanistic estimates, we used one or more generic mechanism species to represent various aspects of their mechanism, combined with their estimated OH radical rate constant. This approach was used for most of the higher molecular weight alcohol, ethers, alcohol ethers, esters, and related compounds present in the inventories. (3) In the estimation of the reactions of the higher molecular weight alcohols, alcohol ethers, or esters, in some cases the reactions of the oxygenated radicals initially formed were estimated to proceed via complex mechanisms which are similar to those predicted to occur in the reactions of the higher molecular weight alkanes. Although we have software for calculating those reactions for the alkanes (see footnotes to Table 6), this software has not been adapted for the analogous calculations for the radicals formed from alcohols, alcohol ethers, or esters. In those cases, we assume that oxygenated radicals react via mechanisms which are calculated for the reactions of normal or branched alkanes with the same numbers of carbons. (The generic mechanism species with designations such as "[N-C7]" or "[BR-C8]", are used for this purpose. They have the same mechanism as that of the corresponding alkane model species listed in Table 6 in the previous section, but their OH radical rate constant is assigned based on that of the oxygenated species whose reactions are being represented.) The mechanistic parameters used for the other generic mechanism species are included in the listing in Table 8.

An example of the use of generic mechanism species to represent an estimated mechanism is provided in the case of the compound 2-ethyl-1-hexanol (SAROAD number 98112). Like other alcohols, it is considered to react significantly only with OH radicals, and its rate of this reaction, both overall and at various positions in the molecule, can be estimated using the techniques of Atkinson (1987). In addition, the procedures and techniques developed by Carter and Atkinson (1985) can be employed to estimate the overall types of products, NO conversions, and radical yields resulting following reaction of OH radicals at the various positions of the molecule. In the case of 2-ethyl-1-hexanol, we estimate that it reacts 30% of the time to form HO<sub>2</sub> + a C<sub>8</sub> aldehyde and the remainder of the time via a mechanism analogous to branched alkanes. This compound is then represented by a mixture of 30% "RCHO-H" (a species which reacts to form HO<sub>2</sub> + RCHO) and 70% [BR-C8] (a species which reacts with the same mechanism as branched C<sub>8</sub> alkanes), with each having the OH radical rate constant estimated for the parent compound. The use of this method to represent the many various alcohols, alcohol ethers, esters, etc., present in the emissions inventories avoided the necessity to add a new detailed model species for each one of these compounds.

#### B. Assignment of Detailed Model Species to Emissions Categories

In order to utilize detailed emissions data as input in airshed model calculations, it is necessary first to determine how the categories of chemical species used in present emissions data bases are to be represented by species in the photochemical mechanisms implemented in the model. The emissions data bases presently employed by the California ARB and by the U. S. EPA give mass emissions of chemical species which are organized using the SAROAD classification system. In this system, a five-digit number is used to designate either individual chemicals, groups of isomeric chemicals which may or may not have similar atmospheric reactivities, or mixtures of chemicals of varying degrees of characterization. As part of this contract, we developed emissions processing software which converts mass emissions of SAROAD classes into molar emissions of species used in the chemical mechanism, and determines the mechanistic parameters for the lumped species which correspond to the emitted species they are representing. This software is documented in detail in a separate report

(Carter 1988). As discussed there, the first step involved in this procedure is to convert the mass emissions of the SAROAD classes into molar emissions of the detailed model species discussed in the previous section. Based on the input data specified by the user which controls how the detailed species are to be lumped for use in the airshed model, the software then determines the emissions of the lumped species in the mechanism, and the parameters to use for those lumped species. In order to carry out this procedure, it is necessary to assign detailed model species to each of the SAROAD classes on the data bases which have non-negligible emissions. This is discussed below.

As a starting point in making the necessary assignments of model species to emissions categories, we obtained from the ARB data sets giving the total emissions into California in the 1983 inventory (Croes and Allen 1987), and we obtained from NCAR data sets giving total emissions into the contiguous United States in the present EPA/NAPAP data base (Middleton 1987). Although both of these data bases use the SAROAD classification system, there are some inconsistencies between them. While many SAROAD classes are common to both systems, there are a large number of SAROAD classes in the EPA/NAPAP set which are not on the 1983 ARB data base, and a smaller number of SAROAD classes used in the ARB set which are not on the EPA/NAPAP data base. A fair number of the EPA classes (particularly the 90xxx series) refer to the same chemicals which are represented by other classes on the data sets. Worse, there are approximately 30 classes where the same SAROAD number is used to represent different chemicals on the ARB data base than they do in the EPA/NAPAP set. The SAROAD classes which are common to both data bases are listed in Table 13; the classes on the EPA, but not the ARB, sets are listed in Table 14; the classes on the ARB, but not the EPA, are listed in Table 15; and the classes where there is an inconsistency between the EPA and the ARB sets are listed in Table 16. These tables also give the weight percent of emissions of the individual classes into California and the contiguous United States given in the respective data sets.

Table 13. Emissions Categories in Both the United States  
 EPA/NAPAP and the 1983 California ARB Emissions  
 Inventories, and Weight Percents of Emissions of  
 these Categories into California or the Contiguous  
 United States

| SAROAD No. | Description               | Weight Percent USA | Weight Percent Calif. |
|------------|---------------------------|--------------------|-----------------------|
| 43105      | ISOMERS OF HEXANE         | 0.2695             | 1.3043                |
| 43106      | ISOMERS OF HEPTANE        | 0.0611             | 1.4199                |
| 43107      | ISOMERS OF OCTANE         | 0.0506             | 1.7034                |
| 43108      | ISOMERS OF NONANE         | 0.4759             | 0.8985                |
| 43109      | ISOMERS OF DECANE         | 0.7633             | 1.4881                |
| 43110      | ISOMERS OF UNDECANE       | 0.1090             | 0.0688                |
| 43113      | ISOMERS OF TETRADECANE    | 0.0126             | 0.0118                |
| 43114      | ISOMERS OF PENTADECANE    | 0.0042             |                       |
| 43115      | C-7 CYCLOPARAFFINS        | 0.7448             | 0.4186                |
| 43116      | C-8 CYCLOPARAFFINS        | 0.0551             | 0.0509                |
| 43117      | C-9 CYCLOPARAFFINS        | 0.0058             | 0.0007                |
| 43118      | MINERAL SPIRITS           | 0.1473             | 0.4515                |
| 43119      | LACTOL SPIRITS            | 0.0024             | 0.0031                |
| 43120      | ISOMERS OF BUTENE         | 0.1015             | 0.7213                |
| 43121      | ISOMERS OF PENTENE        | 0.2014             | 0.4673                |
| 43122      | ISOMERS OF PENTANE        | 0.3512             | 3.1236                |
| 43123      | TERPENES                  | 0.0000             | 0.0318                |
| 43201      | METHANE                   | 12.1822            | 0.1408                |
| 43202      | ETHANE                    | 1.9757             |                       |
| 43203      | ETHYLENE                  | 5.4468             | 0.2990                |
| 43204      | PROPANE                   | 0.5341             | 0.1003                |
| 43205      | PROPENE                   | 1.9086             | 0.0542                |
| 43206      | ACETYLENE                 | 1.5636             | 0.1513                |
| 43208      | PROPADIENE                | 0.0310             | 0.0376                |
| 43209      | METHYLACETYLENE (PROPYNE) | 0.0530             | 0.1829                |
| 43212      | N-BUTANE                  | 4.6553             |                       |
| 43213      | BUTENE                    | 0.5763             | 0.4144                |
| 43214      | ISO-BUTANE                | 1.1450             | 0.0771                |
| 43215      | ISOBUTYLENE               | 0.0093             | 0.0065                |
| 43216      | T-2-BUTENE                | 0.2221             | 0.0043                |
| 43217      | CIS-2-BUTENE              | 0.2010             | 0.8166                |
| 43218      | 1,3-BUTADIENE             | 0.7533             | 0.0742                |
| 43220      | N-PENTANE                 | 1.4673             | 0.1826                |
| 43223      | 3-METHYL-1-BUTENE         | 0.0677             |                       |
| 43224      | 1-PENTENE                 | 0.3877             | 0.0077                |
| 43225      | 2-METHYL-1-BUTENE         | 0.0060             |                       |
| 43226      | TRANS-2-PENTENE           | 0.2651             | 0.0048                |
| 43228      | 2-METHYL-2-BUTENE         | 0.3572             | 0.0077                |
| 43229      | 2-METHYLPENTANE           | 0.6958             |                       |
| 43230      | 3-METHYLPENTANE           | 0.4323             | 0.0056                |
| 43231      | HEXANE                    | 1.4838             | 0.0088                |

(continued)

Table 13 (continued) - 2

| SAROAD<br>No. | Description            | Weight Percent<br>USA | Weight Percent<br>Calif. |
|---------------|------------------------|-----------------------|--------------------------|
| 43232         | HEPTANE                | 1.9581                | 0.0599                   |
| 43233         | OCTANE                 | 0.4197                |                          |
| 43235         | NONANE                 | 0.1765                |                          |
| 43238         | N-DECANE               | 0.1307                |                          |
| 43241         | N-UNDECANE             | 0.3541                | 0.1776                   |
| 43242         | CYCLOPENTANE           | 0.1466                | 0.0195                   |
| 43243         | ISOPRENE               | 0.0014                | 0.0451                   |
| 43245         | 1-HEXENE               | 0.1302                | 0.0374                   |
| 43248         | CYCLOHEXANE            | 0.3058                |                          |
| 43255         | N-DODECANE             | 0.1711                |                          |
| 43258         | N-TRIDECAKE            | 0.0982                | 0.0005                   |
| 43259         | N-TETRADECANE          | 0.0923                | 0.0050                   |
| 43260         | N-PENTADECANE          | 0.9713                | 0.1754                   |
| 43261         | METHYLCYCLOHEXANE      | 0.6408                | 0.0779                   |
| 43262         | METHYLCYCLOPENTANE     | 0.4507                | 0.0150                   |
| 43265         | OCTENE                 | 0.0028                | 0.0054                   |
| 43270         | 3-METHYL-T-2-PENTENE   | 0.0002                |                          |
| 43272         | METHYLCYCLOPENTENE     | 0.0250                | 0.0627                   |
| 43273         | CYCLOHEXENE            | 0.5361                |                          |
| 43277         | 2,4-DIMETHYLHEXANE     | 0.4745                | 0.0048                   |
| 43278         | 2,5-DIMETHYLHEXANE     | 0.0009                | 1.1626                   |
| 43280         | 2,3,3 TRIMETHYLPENTANE | 0.3875                | 0.1336                   |
| 43288         | ETHYLCYCLOHEXANE       | 0.0714                |                          |
| 43289         | C6 OLEFINS             | 0.0014                | 0.1210                   |
| 43291         | 2,2-DIMETHYLBUTANE     | 0.0839                |                          |
| 43292         | CYCLOPENTENE           | 0.1467                | 0.0606                   |
| 43293         | 4-METHYL-T-2-PENTENE   | 0.0010                | 0.0134                   |
| 43294         | C7 OLEFINS             | 0.0007                | 0.0071                   |
| 43295         | 3-METHYLHEXANE         | 0.3674                |                          |
| 43297         | 4-METHYLHEPTANE        | 0.1623                |                          |
| 43298         | 3-METHYLHEPTANE        | 0.1356                | 0.0241                   |
| 43301         | METHYL ALCOHOL         | 0.1727                | 0.0431                   |
| 43302         | ETHYL ALCOHOL          | 2.9615                | 0.0995                   |
| 43303         | N-PROPYL ALCOHOL       | 0.0075                | 0.0000                   |
| 43304         | ISO-PROPYL ALCOHOL     | 2.3109                |                          |
| 43305         | N-BUTYL ALCOHOL        | 0.0461                | 0.0000                   |
| 43306         | ISOBUTYL ALCOHOL       | 0.0043                |                          |
| 43308         | BUTYL CELLOSOLVE       | 0.2182                | 0.0273                   |
| 43309         | TERT-BUTYL ALCOHOL     | 0.0015                | 0.0088                   |
| 43310         | METHYL CELLOSOLVE      | 0.0014                | 0.1069                   |
| 43311         | CELLOSOLVE             | 0.0194                | 0.0236                   |
| 43320         | DIACETONE ALCOHOL      | 0.0001                |                          |
| 43351         | ETHYL ETHER            | 0.0303                | 0.0089                   |
| 43367         | GLYCOL ETHER           | 0.4387                | 0.0215                   |
| 43368         | GLYCOL                 | 0.0050                | 0.0215                   |

(continued)

Table 13 (continued) - 3

| SAROAD<br>No. | Description              | Weight<br>USA | Percent<br>Calif. |
|---------------|--------------------------|---------------|-------------------|
| 43369         | PROPYLENE GLYCOL         | 0.2412        | 0.0028            |
| 43370         | ETHYLENE GLYCOL          | 0.0801        | 0.1501            |
| 43371         | HEXYLENE GLYCOL          | 0.0019        |                   |
| 43404         | ACETIC ACID              | 0.0852        | 0.2032            |
| 43432         | METHYLACETATE            | 0.0660        |                   |
| 43433         | ETHYL ACETATE            | 0.1445        |                   |
| 43434         | N-PROPYL ACETATE         | 0.2148        |                   |
| 43435         | N-BUTYL ACETATE          | 0.7747        | 0.0222            |
| 43438         | ETHYL ACRYLATE           | 0.0138        | 1.6146            |
| 43444         | ISOPROPYL ACETATE        | 0.2436        | 0.0508            |
| 43446         | ISOBUTYL ACETATE         | 0.0071        | 0.0034            |
| 43450         | DIMETHYL FORMAMIDE       | 0.0017        | 0.3868            |
| 43451         | ISOBUTYL ISOBUTRYATE     | 0.0298        |                   |
| 43452         | CELLOSOLVE ACETATE       | 0.0131        | 0.9432            |
| 43502         | FORMALDEHYDE             | 1.3747        |                   |
| 43503         | ACETALDEHYDE             | 0.3497        |                   |
| 43504         | PROPIONALDEHYDE          | 0.0171        |                   |
| 43505         | ACROLEIN                 | 0.0757        |                   |
| 43510         | BUTYRALDEHYDE            | 0.0162        | 0.1082            |
| 43512         | HEXANAL                  | 0.0019        |                   |
| 43551         | ACETONE                  | 0.9037        |                   |
| 43552         | METHYL ETHYL KETONE      | 0.4677        |                   |
| 43559         | METHYL BUTYL KETONE      | 0.0033        | 0.1642            |
| 43560         | METHYL ISOBUTYL KETONE   | 0.1194        |                   |
| 43601         | ETHYLENE OXIDE           | 0.0223        | 0.0073            |
| 43602         | PROPYLENE OXIDE          | 0.0081        | 0.0024            |
| 43704         | ACRYLONITRILE            | 0.0853        | 0.0413            |
| 43721         | ETHYLAMINE               | 0.0000        | 0.0003            |
| 43740         | TRIMETHYLAMINE           | 0.0000        | 0.0166            |
| 43801         | METHYL CHLORIDE          | 0.0040        |                   |
| 43802         | DICHLOROMETHANE          | 0.3120        | 0.0075            |
| 43803         | CHLOROFORM               | 0.0024        | 0.0155            |
| 43804         | CARBON TETRACHLORIDE     | 0.0071        | 0.0202            |
| 43811         | TRICHLOROFLUOROMETHANE   | 0.0207        | 0.0272            |
| 43812         | ETHYL CHLORIDE           | 0.0522        |                   |
| 43814         | 1,1,1-TRICHLOROETHANE    | 0.5624        | 0.0011            |
| 43815         | ETHYLENE DICHLORIDE      | 0.1528        | 0.0001            |
| 43817         | PERCHLOROETHYLENE        | 1.5167        | 0.0211            |
| 43820         | 1,1,2-TRICHLOROETHANE    | 0.0016        |                   |
| 43821         | TRICHLOROTRIFLUOROETHANE | 0.1389        | 0.0058            |
| 43822         | TRIMETHYLFLUOROSILANE    | 0.0270        |                   |
| 43823         | DICHLORODIFLUOROMETHANE  | 0.0264        |                   |
| 43824         | TRICHLOROETHYLENE        | 0.5722        | 0.0011            |
| 43860         | VINYL CHLORIDE           | 0.1694        | 0.0226            |
| 45101         | NAPHTHA                  | 0.9061        | 0.0033            |

(continued)

Table 13 (continued) - 4

| SAROAD<br>No. | Description               | Weight Percent<br>USA | Weight Percent<br>Calif. |
|---------------|---------------------------|-----------------------|--------------------------|
| 45102         | ISOMERS OF XYLENE         | 0.5690                |                          |
| 45104         | ISOMERS OF ETHYLtolUENE   | 0.0142                |                          |
| 45105         | ISOMERS OF BUTYLBENZENE   | 0.2396                | 0.0247                   |
| 45106         | ISOMERS OF DIETHYLBENZENE | 0.0139                |                          |
| 45107         | TRIMETHYLBENZENE          | 0.2497                | 0.0213                   |
| 45201         | BENZENE                   | 2.3314                |                          |
| 45202         | TOLUENE                   | 5.4344                | 0.0008                   |
| 45203         | ETHYLBENZENE              | 0.5924                | 0.0018                   |
| 45204         | O-XYLENE                  | 1.1046                |                          |
| 45205         | M-XYLENE                  | 0.2507                |                          |
| 45206         | P-XYLENE                  | 0.9167                |                          |
| 45207         | 1,3,5-TRIMETHYLBENZENE    | 0.7686                |                          |
| 45208         | 1,2,4-TRIMETHYLBENZENE    | 0.8354                |                          |
| 45209         | N-PROPYLBENZENE           | 0.1724                | 4.5481                   |
| 45211         | O-ETHYLtolUENE            | 0.0002                | 0.2415                   |
| 45212         | M-ETHYLtolUENE            | 0.1090                |                          |
| 45215         | TERT-BUTYLBENZENE         | 0.0007                |                          |
| 45216         | S-BUTYLBENZENE            | 0.0394                | 2.0284                   |
| 45220         | STYRENE                   | 0.2304                | 0.0259                   |
| 45221         | METHYL STYRENE            | 0.1237                | 0.0012                   |
| 45225         | 1,2,3-TRIMETHYLBENZENE    | 0.2351                | 0.0007                   |
| 45401         | XYLENE BASE ACIDS         | 0.0058                |                          |
| 45402         | BENZOIC ACID              | 0.0050                | 0.0048                   |
| 45801         | CHLOROBENZENE             | 0.1245                |                          |
| 45807         | P-DICHLOROBENZENE         | 0.0535                |                          |
| 98033         | 2,2,5-TRIMETHYLHEXANE     | 0.1658                |                          |
| 98034         | T-2-HEXENE                | 0.0016                |                          |
| 98035         | C-2-HEXENE                | 0.0047                |                          |
| 98040         | 2-METHYL-1-PENTENE        | 0.0002                |                          |
| 98041         | 3-HEPTENE                 | 0.0001                |                          |
| 98044         | INDANE                    | 0.2088                |                          |
| 98054         | 2,4,4-TRIMETHYL-1-PENTENE | 0.0540                |                          |
| 98056         | ISOVALERALDEHYDE          | 0.0000                |                          |
| 98057         | ETHYLCYCLOPENTANE         | 0.0196                |                          |
| 98058         | TRIMETHYLCYCLOPENTANE     | 0.0348                |                          |
| 98059         | DIMETHYLCYCLOHEXANE       | 0.1698                |                          |
| 98060         | TRIMETHYLCYCLOHEXANE      | 0.0764                |                          |
| 98062         | DIETHYLCYCLOHEXANE        | 0.2056                |                          |
| 98063         | N-PENTYLCYCLOHEXANE       | 0.0073                |                          |
| 98082         | ETHYLHEPTENE              | 0.0583                |                          |
| 98083         | TRIMETHYLDECENE           | 0.0166                |                          |
| 98090         | METHYLHEPTENE             | 0.0111                |                          |
| 98091         | DIMETHYLHEPTANE           | 0.0313                |                          |
| 98106         | ETHYLISOPROPYL ETHER      | 0.0005                |                          |

Table 14. Emissions Categories which are in the EPA/NAPAP Emissions Data Base but which are not used in the 1983 California Inventory, and Weight Percents of Emissions of these Categories into the Contiguous United States

| SAROAD No. | Description                 | Weight Percent |
|------------|-----------------------------|----------------|
| 43124      | C9 OLEFINS                  | 0.0128         |
| 43125      | C10 OLEFINS                 | 0.2009         |
| 43126      | C2 CYCLOHEXANE              | 0.0736         |
| 43127      | C3 CYCLOHEXANE              | 0.0507         |
| 43128      | C5 CYCLOHEXANE              | 0.0232         |
| 43129      | C4 SUBSTITUTED CYCLOHEXANE  | 0.0736         |
| 43130      | C5 SUBSTITUTED CYCLOHEXANE  | 0.0123         |
| 43131      | C6 SUBSTITUTED CYCLOHEXANE  | 0.0092         |
| 43132      | ALIPHATICS                  | 0.0073         |
| 43133      | PARAFFINS (C16-C34)         | 0.0012         |
| 43134      | PARAFFINS/OLEFINS (C12-C16) | 0.0001         |
| 43135      | C10 PARAFFIN                | 0.0566         |
| 43136      | C9 PARAFFIN                 | 0.0220         |
| 43137      | C16 BRANCHED ALKANE         | 0.0013         |
| 43138      | C-8 OLEFINS                 | 0.0177         |
| 43140      | C7-C16                      | 0.0073         |
| 43141      | C8 PARAFFIN                 | 0.1761         |
| 43142      | C7 PARAFFIN                 | 0.0018         |
| 43143      | C5 OLEFIN                   | 0.0876         |
| 43144      | C5 PARAFFIN                 | 0.0959         |
| 43145      | C5 PARAFFIN/OLEFIN          | 0.0495         |
| 43146      | C11 OLEFIN                  | 0.0067         |
| 43147      | C12 OLEFIN                  | 0.0006         |
| 43148      | C9H16                       | 0.0040         |
| 43150      | C10H18                      | 0.1135         |
| 43151      | C11H20                      | 0.0003         |
| 43153      | C10H16                      | 0.0001         |
| 43155      | ISOMERS OF HEPTADECANE      | 0.0286         |
| 43156      | ISOMERS OF OCTADECANE       | 0.0131         |
| 43221      | ISO PENTANE                 | 2.5978         |
| 43247      | 2,4-DIMETHYLPENTANE         | 0.2870         |
| 43250      | 2,2,4-TRIMETHYLPENTANE      | 0.6905         |
| 43252      | 2,3,4-TRIMETHYLPENTANE      | 0.0498         |
| 43254      | ISOOCTANE                   | 0.0340         |
| 43256      | A-PINENE                    | 0.0560         |
| 43257      | B-PINENE                    | 0.0366         |
| 43313      | 1-ETHOXY-2-PROPANOL         | 0.0001         |
| 43314      | S-BUTYL ALCOHOL             | 0.0418         |
| 43317      | CYCLOHEXANOL                | 0.0041         |
| 43318      | 2-ETHYL HEXANOL             | 0.0004         |
| 43321      | 2-ETHYL-1-HEXANOL           | 0.0001         |

(continued)

Table 14 (continued) - 2

| SAROAD<br>No. | Description                  | Weight Percent |
|---------------|------------------------------|----------------|
| 43330         | ISOAMYL ALCOHOL              | 0.0001         |
| 43331         | DIMETHYLPENTANOL             | 0.0032         |
| 43332         | DIMETHYLOCTANOL              | 0.0005         |
| 43333         | DIMETHYLHEPTANOL             | 0.0003         |
| 43334         | METHYLHEPTANOL               | 0.0005         |
| 43335         | METHOXYETHOXETHANOL          | 0.0003         |
| 43336         | OCTANOL                      | 0.0001         |
| 43337         | BUTOXYETHOXETHANOL           | 0.0045         |
| 43350         | DIMETHYLETHER                | 0.2391         |
| 43372         | DIBUTYL ETHER                | 0.0000         |
| 43373         | DIETHYLENE GLYCOL            | 0.0014         |
| 43374         | DIPROPYLENE GLYCOL           | 0.0023         |
| 43376         | METHYL T-BUTYL ETHER         | 0.0012         |
| 43377         | CARBITOL                     | 0.0166         |
| 43378         | METHYL CARBITOL              | 0.0014         |
| 43379         | BUTYL CARBITOL               | 0.0014         |
| 43391         | 2-BUTYLtetrahydrofuran       | 0.0000         |
| 43395         | C7H12O                       | 0.0018         |
| 43397         | TRIMETHYLCYCLOHEXANOL        | 0.0004         |
| 43403         | FORMIC ACID                  | 0.0043         |
| 43405         | PROPIONIC ACID               | 0.0014         |
| 43407         | ACRYLIC ACID                 | 0.0016         |
| 43408         | PALMITIC ACID                | 0.0380         |
| 43409         | ADIPIC ACID                  | 0.0289         |
| 43410         | HEXADECANOIC ACID            | 0.0001         |
| 43430         | METHYL FORMATE               | 0.0176         |
| 43437         | METHYL ACRYLATE              | 0.0013         |
| 43440         | BUTYL ACRYLATE               | 0.0051         |
| 43441         | METHYL METHACRYLATE          | 0.0801         |
| 43453         | VINYL ACETATE                | 0.0413         |
| 43454         | METHYL PALMITATE             | 0.0087         |
| 43455         | METHYL MYRISTATE             | 0.0013         |
| 43456         | METHYL STEARATE              | 0.0110         |
| 43457         | METHYLAL                     | 0.0093         |
| 43458         | SUBSTITUTED C9 ESTER (C12)   | 0.0027         |
| 43459         | C5 ESTER                     | 0.0646         |
| 43460         | METHYL C11 ESTER             | 0.0000         |
| 43461         | METHYL C12 ESTER             | 0.0000         |
| 43462         | METHYL C13 ESTER             | 0.0000         |
| 43463         | METHYL C14 ESTER             | 0.0001         |
| 43464         | METHYL C15 ESTER             | 0.0000         |
| 43465         | METHYL C19 ESTER             | 0.0000         |
| 43466         | METHYL C20 ESTER             | 0.0000         |
| 43467         | C4 SUBSTITUTED CYCLOHEXANONE | 0.0070         |
| 43468         | ISOBUTYL ACRYLATE            | 0.0013         |

(continued)

Table 14 (continued) - 3

| SAROAD<br>No. | Description                  | Weight Percent |
|---------------|------------------------------|----------------|
| 43469         | BUTOXYETHOXYETHANOL ACETATE  | 0.0255         |
| 43470         | METHYL DODECANOATE           | 0.0000         |
| 43472         | DIMETHYLPENTANEDIOATE        | 0.0138         |
| 43473         | ETHYLHEXANOATE               | 0.0009         |
| 43474         | METHYLMETHYLPROPENOATE       | 0.0028         |
| 43475         | METHYLETHYL PENTANOATE       | 0.0002         |
| 43476         | DIMETHYLHEXANEDIOATE         | 0.0006         |
| 43477         | DIMETHYLPENTANEDIOATE        | 0.0064         |
| 43514         | METHYL GLYOXAL               | 0.0181         |
| 43515         | CROTONALDEHYDE               | 0.0069         |
| 43520         | TOTAL C2-C5 ALDEHYDES        | 0.0081         |
| 43562         | METHYL AMYL KETONE           | 0.0019         |
| 43563         | 2-METHYL-3-HEXANONE          | 0.1924         |
| 43564         | HEPTANONE                    | 0.0425         |
| 43565         | DIMETHYLCYCLOBUTANONE        | 0.0038         |
| 43566         | TRIMETHYLCYCLOPENTANONE      | 0.0003         |
| 43567         | TETRAMETHYLPENTANONE         | 0.0116         |
| 43568         | NONENONE                     | 0.0534         |
| 43570         | ALKENE KETONE                | 0.0507         |
| 43603         | MALEIC ANHYDRIDE             | 0.0067         |
| 43604         | ACETIC ANHYDRIDE             | 0.0082         |
| 43650         | OXYGENATES                   | 0.0002         |
| 43776         | HEXAMETHYLENEDIAMINE         | 0.0689         |
| 43777         | ETHANOLAMINE                 | 0.0035         |
| 43778         | ETHYLENEAMINES               | 0.0016         |
| 43780         | DIMETHYL ALKYL AMINES        | 0.0004         |
| 43835         | 1-CHLOROBUTANE               | 0.0002         |
| 43836         | 3-(CHLOROMETHYL)-HEPTANE     | 0.0001         |
| 43837         | ETHYLENE DIBROMIDE           | 0.0246         |
| 43838         | PROPYLENE DICHLORIDE         | 0.0014         |
| 43839         | TETRAFLUOROMETHANE           | 0.0025         |
| 43840         | CHLORODIFLUOROMETHANE        | 0.0119         |
| 43841         | DICHLOROTETRAFLUORETHANE     | 0.0011         |
| 43842         | CHLOROPENTAFLUOROETHANE      | 0.0012         |
| 43843         | HEXAFLUOROETHANE             | 0.0299         |
| 43844         | TRIFLUOROMETHANE             | 0.0227         |
| 43845         | CHLOROTRIFLUOROMETHANE       | 0.0040         |
| 43862         | CHLOROPRENE                  | 0.0252         |
| 43863         | EPICHLOROHYDRIN              | 0.0015         |
| 43902         | ETHYL MERCAPTAN              | 0.0012         |
| 43933         | CARBONYL SULFIDE             | 0.0714         |
| 43934         | CARBON SULFIDE               | 0.2144         |
| 43950         | OCTAMETHYLCYCLOTETRASILOXANE | 0.0003         |
| 43951         | SILOXANE                     | 0.0002         |
| 45109         | C3/C4/C5 ALKYL BENZENES      | 0.0026         |

(continued)

Table 14 (continued) - 4

| SAROAD<br>No. | Description                | Weight Percent |
|---------------|----------------------------|----------------|
| 45110         | C10 AROMATIC               | 0.6939         |
| 45111         | C10H12                     | 0.0018         |
| 45151         | (NO LABEL)                 | 0.0003         |
| 45210         | CUMENE (ISOPROPYL BENZENE) | 0.0179         |
| 45217         | 1,2 DIETHYLBENZENE         | 0.2121         |
| 45218         | M-DIETHYLBENZENE           | 0.2099         |
| 45226         | BIPHENYL                   | 0.0010         |
| 45227         | METHYL BIPHENYL            | 0.0001         |
| 45228         | ETHYL STYRENE              | 0.0014         |
| 45229         | DIVINYL BENZENE            | 0.0001         |
| 45230         | DI(ETHYLPHENYL) ETHANE     | 0.0000         |
| 45231         | PENTYL BENZENE             | 0.0018         |
| 45235         | BUTYL BENZENE              | 0.0088         |
| 45236         | DIISOPROPYL BENZENE        | 0.0013         |
| 45238         | ETHYLTOLUENE               | 0.1664         |
| 45240         | PROPYLBENZENE              | 0.0463         |
| 45241         | 4-PHENYL-1-BUTENE          | 0.0081         |
| 45242         | T-1-PHENYLBUTENE           | 0.0072         |
| 45243         | ETHYLDIMETHYLBENZENE       | 0.0569         |
| 45244         | TETRAMETHYLBENZENE         | 0.0472         |
| 45245         | C5-ALKYLBENZENE            | 0.0781         |
| 45246         | C5-ALKYLBENZENE (UNSAT.)   | 0.0023         |
| 45247         | C6-ALKYLBENZENE            | 0.0052         |
| 45248         | C4-ALKYLSYRENE             | 0.0032         |
| 45303         | C4-ALKYLPHENOL             | 0.0018         |
| 45304         | C5-ALKYLPHENOL             | 0.0023         |
| 45310         | C8 PHENOLS                 | 0.0001         |
| 45311         | C9 PHENOLS                 | 0.0002         |
| 45320         | DIMETHYLBENZYLALCOHOL      | 0.0008         |
| 45330         | BIPHENYLOL                 | 0.0005         |
| 45403         | TEREPHTHALIC ACID          | 0.0003         |
| 45404         | DIMETHYLETHYLBENZOICACID   | 0.0001         |
| 45451         | DIMETHYL PHTHALATE         | 0.0053         |
| 45452         | DIBUTYL PHTHALATE          | 0.0779         |
| 45454         | DIPROPYL PHTHALATE         | 0.0000         |
| 45455         | BUTYL BENZOATE             | 0.0245         |
| 45456         | BUTYLISOPROPYLPHthalate    | 0.0990         |
| 45470         | DI-C8 ALKYL PHTHALATE      | 0.0028         |
| 45477         | (NO LABEL)                 | 0.0092         |
| 45501         | BENZALDEHYDE               | 0.0531         |
| 45502         | P-TOLUALDEHYDE             | 0.0267         |
| 45503         | 2-FURFURAL                 | 0.0730         |
| 45601         | PHTHALIC ANHYDRIDE         | 0.0403         |
| 45604         | FURFURYL ALCOHOL           | 0.0000         |
| 45605         | CRESOL                     | 0.0013         |

(continued)

Table 14 (continued) - 5

| SAROAD<br>No. | Description                                     | Weight Percent |
|---------------|---|----------------|
| 45701         | ANILINE   | 0.0282         |
| 45702         | NITROBENZENE                                    | 0.0012         |
| 45703         | 2,2 DICHLORONITROANILINE                        | 0.0118         |
| 45704         | BROMODINITROANALINE                             | 0.0000         |
| 45705         | BROMODINITROBENZENE                             | 0.0011         |
| 45706         | N-PHENYLANILINE                                 | 0.0003         |
| 45731         | TOLUENE DIISOCYANATE                            | 0.0030         |
| 45740         | TOTAL AROMATIC AMINES                           | 0.0025         |
| 45750         | PIPERYLENE                                      | 0.0014         |
| 45805         | O-DICHLOROBENZENE                               | 0.0756         |
| 45806         | M-DICHLOROBENZENE                               | 0.0002         |
| 45808         | DICHLOROBENZENES                                | 0.0015         |
| 45830         | TRICHLOROBENZENES                               | 0.0005         |
| 45831         | TETRACHLOROBENZENES                             | 0.0000         |
| 46102         | ANTHRAQUINONE                                   | 0.0014         |
| 46103         | AMINOANTHRAQUINONE                              | 0.0000         |
| 46110         | METHYLENEBIS(C <sub>6</sub> H <sub>4</sub> NCO) | 0.0000         |
| 46111         | 4,4'-METHYLENE DIANILINE                        | 0.0000         |
| 46112         | PHENYL ISOCYANATE                               | 0.0089         |
| 46114         | 4-METHYLANILINE                                 | 0.0021         |
| 46115         | DIMETHYLNAPHTHYRIDINE                           | 0.0005         |
| 46202         | OCTAHYDROINDENE                                 | 0.0012         |
| 46210         | CREOSOTE  | 0.0730         |
| 46601         | TETRAMETHYLTHIOUREA                             | 0.0004         |
| 46602         | BENZOTHIAZOLE                                   | 0.0001         |
| 46701         | NAPTHALENE                                      | 0.0754         |
| 46702         | METHYLNAPHTHALENES                              | 0.0664         |
| 46703         | DIMETHYLNAPTHALENE                              | 0.0002         |
| 46705         | ACENAPHTHYLENE                                  | 0.0001         |
| 46706         | ACENAPHTHENE                                    | 0.0000         |
| 46707         | FLUORENE  | 0.0000         |
| 46708         | PHENANTHRENE                                    | 0.0002         |
| 46710         | FLUORANTHENE                                    | 0.0000         |
| 46711         | C <sub>2</sub> ALKYL INDAN                      | 0.0332         |
| 46712         | INDENE  | 0.0000         |
| 46713         | PYRENE  | 0.0000         |
| 46714         | BENZO(g,h,i)FLUORANTHENE                        | 0.0000         |
| 46715         | CHRYSENE  | 0.0000         |
| 46717         | BENZO(b)FLUORANTHENE                            | 0.0000         |
| 46746         | C <sub>2</sub> -ALKYLNAPTHALENE                 | 0.0046         |
| 46747         | METHYLINDAN                                     | 0.0243         |
| 46748         | METHYLDECALIN                                   | 0.0018         |
| 46749         | METHYLDIHYDRONAPHTHALENE                        | 0.0005         |
| 46750         | DIMETHYLINDAN                                   | 0.0197         |
| 46751         | DIHYDRONAPTHALENE                               | 0.0028         |

(continued)

Table 14 (continued) - 6

| SAROAD<br>No. | Description                 | Weight Percent |
|---------------|-----------------------------|----------------|
| 46752         | DIMETHYLINDENE              | 0.0005         |
| 46753         | DECALIN                     | 0.0027         |
| 46754         | ETHYLINDAN                  | 0.0018         |
| 46755         | TRIMETHYLINDAN              | 0.0028         |
| 90001         | DODECENE                    | 0.0018         |
| 90002         | 2,3,5-TRIMETHYLHEXANE       | 0.0335         |
| 90003         | 2,4 DIMETHYLHEPTANE         | 0.0403         |
| 90005         | 2,5 DIMETHYLHEPTANE         | 0.2549         |
| 90008         | 2-METHYLOCTANE              | 0.0047         |
| 90009         | 2,4,5-TRIMETHYLHEPTANE      | 0.0895         |
| 90010         | M-XYLENE AND P-XYLENE       | 0.7271         |
| 90011         | METHYLALLENE                | 0.0014         |
| 90013         | C-2-OCTENE                  | 0.0001         |
| 90014         | 1-DECENE                    | 0.0050         |
| 90015         | 3-METHYLOCTANE              | 0.0097         |
| 90016         | 4-METHYLOCTANE              | 0.0121         |
| 90017         | METHYLCYCLOOCTANE           | 0.0103         |
| 90019         | C6H18O3S13                  | 0.0785         |
| 90020         | C8H24O4S14                  | 0.0263         |
| 90021         | METHYLPROPANE               | 0.1215         |
| 90022         | METHYLPROPENE               | 0.0064         |
| 90023         | METHYLBUTENE                | 0.0028         |
| 90024         | METHYLBUTADIENE             | 0.0005         |
| 90025         | METHYLPENTENE               | 0.0408         |
| 90026         | METHYLPENTANE               | 0.0807         |
| 90027         | METHYLCYCLOPENTADIENE       | 0.0018         |
| 90028         | METHYLHEXANE                | 0.1254         |
| 90029         | METHYLHEXENE                | 0.0043         |
| 90030         | HEXADECANE                  | 0.0269         |
| 90031         | N-HEPTADECANE               | 0.0001         |
| 90032         | 1-UNDECENE                  | 0.0044         |
| 90033         | CYCLOPENTYL CYCLOPENTANE    | 0.0143         |
| 90034         | T-2-NONENE                  | 0.0053         |
| 90036         | PENTYNE                     | 0.0059         |
| 90037         | HEXYNE                      | 0.0006         |
| 90038         | CIS-1,4 DIMETHYLCYCLOHEXANE | 0.0025         |
| 90039         | METHYLHEXADIENE             | 0.0115         |
| 90041         | METHYLCYCLOHEXADIENE        | 0.0009         |
| 90042         | T-3-HEXENE                  | 0.0995         |
| 90043         | METHYLHEXANAL               | 0.0422         |
| 90044         | METHYLHEPTYNE               | 0.0009         |
| 90045         | METHYLHEPTANE               | 0.0160         |
| 90046         | METHYLCYCLOHEXENE           | 0.0064         |
| 90047         | METHYLNONANE                | 0.0390         |
| 90048         | METHYLDECANE                | 0.0265         |

(continued)

Table 14 (continued) - 7

| SAROAD<br>No. | Description                | Weight Percent |
|---------------|----------------------------|----------------|
| 90049         | METHYLUNDECANE             | 0.0159         |
| 90050         | CAMPHENENE                 | 0.0013         |
| 90051         | MYRCENE                    | 0.0020         |
| 90052         | B-PHELLANDRENE             | 0.0018         |
| 90053         | D-LIMONENE                 | 0.0085         |
| 90054         | PENTENYNE                  | 0.0014         |
| 90055         | PENTYLCYCLOHEXANE          | 0.0010         |
| 90056         | HEXENE                     | 0.0183         |
| 90058         | HEXDIEINAL                 | 0.0014         |
| 90059         | HEPTADIENAL                | 0.0009         |
| 90060         | DIMETHYLBUTANE             | 0.1050         |
| 90061         | DIMETHYLBUTENE             | 0.0138         |
| 90062         | DIMETHYLPENTANE            | 0.0165         |
| 90063         | DIMETHYLPENTENE            | 0.0009         |
| 90064         | DIMETHYLCYCLOPENTANE       | 0.0308         |
| 90065         | DIMETHYLCYCLOPENTENE       | 0.0142         |
| 90066         | NONADIENE                  | 0.0009         |
| 90067         | DIMETHYLHEXANE             | 0.0430         |
| 90068         | DIMETHYLHEXDIEINE          | 0.0046         |
| 90069         | DIMETHYLETHYLCYCLOHEXANE   | 0.0041         |
| 90070         | DIMETHYLOCTANE             | 0.0249         |
| 90071         | DIMETHYLUNDECANE           | 0.0025         |
| 90072         | METHYLPROPYLCYCLOHEXANE    | 0.0116         |
| 90073         | METHYLISOPROPYLCYCLOHEXANE | 0.0015         |
| 90074         | DIMETHYLDECANE             | 0.0038         |
| 90075         | ETHYLOCTENE                | 0.0010         |
| 90076         | DIMETHYLNONANE             | 0.0126         |
| 90077         | ETHYLOCTANE                | 0.0043         |
| 90078         | ETHYLPENTENE               | 0.0014         |
| 90079         | ETHYLCYCLOPENTENE          | 0.0028         |
| 90080         | ETHYLMETHYLCYCLOPENTANE    | 0.0068         |
| 90081         | ETHYLHEXANE                | 0.0549         |
| 90082         | ETHYLMETHYLHEXANE          | 0.0098         |
| 90083         | ETHYLMETHYLCYCLOHEXANE     | 0.0368         |
| 90084         | ETHYLHEPTANE               | 0.0009         |
| 90085         | ETHYLMETHYLOCTANE          | 0.0026         |
| 90086         | ETHYLBICYCLOHEPTANE        | 0.0005         |
| 90087         | ETHYLDIMETHYLPENTANE       | 0.0060         |
| 90089         | ETHYLDIMETHYL CYCLOHEXANE  | 0.0023         |
| 90090         | ETHYLPROPYLCYCLOHEXANE     | 0.0026         |
| 90091         | TETRAMETHYLCYCLOBUTENE     | 0.0018         |
| 90092         | TRIMETHYLPENTANE           | 0.0312         |
| 90093         | TRIMETHYLPENTADIENE        | 0.0023         |
| 90094         | TRIMETHYLHEPTANE           | 0.0243         |
| 90095         | TRIMETHYLHEXENE            | 0.0025         |

(continued)

Table 14 (continued) - 8

| SAROAD<br>No. | Description                 | Weight Percent |
|---------------|-----------------------------|----------------|
| 90096         | TRIMETHYLOCTANE             | 0.0114         |
| 90097         | TRIMETHYLDECANE             | 0.0037         |
| 90098         | TETRAMETHYLCYCLOPENTANE     | 0.0028         |
| 90099         | OCTATRIENE                  | 0.0005         |
| 90100         | NONENE                      | 0.0014         |
| 90101         | BUTYLCYCLOHEXANE            | 0.0075         |
| 90102         | METHYLPROPYLNONANE          | 0.0007         |
| 90103         | PENTADIENE                  | 0.0018         |
| 90104         | METHYLOCTANE                | 0.0559         |
| 90105         | PROPYENYL CYCLOHEXANE       | 0.0036         |
| 90106         | METHYLNONENE                | 0.0007         |
| 90107         | METHYLDECENE                | 0.0033         |
| 90108         | METHYLDODECANE              | 0.0005         |
| 90109         | PROPYLHEPTENE               | 0.0011         |
| 90110         | DIETHYLMETHYLCYCLOHEXANE    | 0.0011         |
| 90111         | ISOPROPYLMETHYLCYCLOHANE    | 0.0010         |
| 90112         | DIMETHYLOCTYNE              | 0.0001         |
| 90113         | PENTYLIDENE CYCLOHEXANE     | 0.0004         |
| 90114         | DIMETHYLBUTYLCYCLOHEXANE    | 0.0001         |
| 90115         | TRIMETHYLHEXANE             | 0.0059         |
| 90117         | LIMONENE                    | 0.0009         |
| 90118         | OCTAHYDRO PENTALENE         | 0.0001         |
| 90120         | PROPYLCYCLOHEXANE           | 0.0046         |
| 90122         | TETRAMETHYLHEXANE           | 0.0006         |
| 90125         | HENEICOSANE                 | 0.0023         |
| 90126         | EICOSANE                    | 0.0037         |
| 90127         | NONADECANE                  | 0.0069         |
| 90128         | ISOPROPYLCYCLOHEXANE        | 0.0025         |
| 90130         | CARYOPHYLLENE               | 0.0009         |
| 99098         | (NO LABEL)                  | 0.0162         |
| 99909         | 2,6 DIMETHYLOCTANE          | 0.0022         |
| 99910         | 2,4 DIMETHYLOCTANE          | 0.0241         |
| 99911         | 3,4 DIMETHYLOCTANE          | 0.2543         |
| 99912         | 1-METHYL-3-ETHYL BENZENE    | 0.3691         |
| 99913         | 1-METHYL-2-ETHYL BENZENE    | 0.0723         |
| 99915         | ISOBUTYL BENZENE            | 0.1889         |
| 99916         | 1-METHYL-3-N-PROPYLBENZENE  | 0.0635         |
| 99917         | 1-METHYL-3-ISOPROPYLBENZENE | 0.1304         |
| 99918         | 2-METHYLDECANE              | 0.3906         |
| 99933         | DENATURANT                  | 0.0073         |
| 99999         | UNIDENTIFIED                | 5.8341         |

Table 15. Emissions Categories which are in the 1983 California Emissions Data Base but which are not used in the EPA/NAPAP Inventory, and Weight Percents of Emissions of these Categories into California

| SAROAD<br>No. | Description                    | Weight Percent |
|---------------|--------------------------------|----------------|
| 43207         | CYCLOPROPANE                   |                |
| 43211         | 3-METHYL-1-PENTENE             |                |
| 43219         | ETHYLACETYLENE                 |                |
| 43234         | 2,3-DIMETHYL-1-BUTENE          |                |
| 99905         | ISOMERS OF HEXENE              |                |
| 99901         | 1-OCTENE                       |                |
| 43266         | C-2-OCTENE                     | 0.0048         |
| 99906         | ISOMERS OF OCTENE              |                |
| 43267         | 1-NONENE                       | 0.0077         |
| 43268         | 1-DECENE                       |                |
| 43274         | 2,3-DIMETHYLPENTANE            |                |
| 43279         | 2,3,4-TRIMETHYLPENTANE         | 0.0374         |
| 43290         | C8 OLEFINS                     | 0.1754         |
| 43299         | 2,2,5-TRIMETHYLPENTANE         |                |
| 43390         | TETRAHYDROFURAN                |                |
| 43443         | CELLOSOLVE ACETATE             |                |
| 43445         | METHYL AMYL ACETATE            |                |
| 43702         | ACETONITRILE                   |                |
| 43805         | METHYLENE BROMIDE              | 0.2281         |
| 43807         | CARBON TETRABROMIDE            |                |
| 43813         | 1,1-DICHLOROETHANE             | 0.0004         |
| 43825         | CHLORODIFLUOROMETHANE (F-22)   |                |
| 43826         | CHLOROTRIFLUOROMETHANE (F-13)  |                |
| 43827         | CHLOROPENTAFLUOROETHANE(F-115) |                |
| 43828         | DICHLOROTETRAFLUOROETHANE/114  |                |
| 43830         | CHLOROFLUOROHYDROCARBONS       |                |
| 43850         | PHOSGENE (CCL20)               |                |
| 45103         | DIMETHYLETHYLBENZENE           |                |
| 45234         | METHYLPROPYLBENZENE            |                |
| 98001         | 2,3-DIMETHYLBUTANE             |                |
| 98002         | 2-ETHYL-1-BUTENE               |                |
| 98003         | C-3-HEXENE                     |                |
| 98004         | 2-METHYL-2-PENTENE             |                |
| 98005         | 1-HEPTENE                      | 0.1082         |
| 98010         | METHYLNAPHTHALENE              | 0.0387         |
| 98011         | ETHYLNAPHTHALENE               |                |
| 98012         | DIMETHYLNAPHTHALENE            |                |
| 98013         | PROPYLNAPHTHALENE              |                |
| 98014         | TRIMETHYLNAPHTHALENE           |                |
| 98015         | ANTHRACENE                     |                |
| 98016         | METHYLANTHRACENE               |                |
| 98017         | DM-2,3,DH-1H-INDENE            |                |

(continued)

Table 15 (continued) - 2

| SAROAD<br>No. | Description                  | Weight Percent |
|---------------|------------------------------|----------------|
| 98018         | DIMETHYL ETHER               | 0.1642         |
| 98019         | CRYOFLUORANE (F 114)         |                |
| 98020         | B-METHYLSTYRENE              |                |
| 98021         | O-CRESOL (2-M-BENZENOL)      |                |
| 98022         | M-CRESOL (3-M-BENZENOL)      |                |
| 98023         | P-CRESOL (4-M-BENZENOL)      |                |
| 98025         | A-PINENE                     | 0.0144         |
| 98026         | B-PINENE                     | 0.0135         |
| 98027         | D-LIMONENE                   | 0.0156         |
| 98028         | PHTHALIC ANAHYDRIDE          |                |
| 98030         | CARBON SULFIDE               | 0.0073         |
| 98031         | CARBONYL SULFIDE             | 0.0024         |
| 98032         | 3,5,5-TRIMETHYLHEXANE        | 0.0622         |
| 98036         | ISOBUTYRALDEHYDE             | 0.0003         |
| 98038         | C9 OLEFINS                   | 0.0296         |
| 98039         | C10 OLEFINS                  | 0.0054         |
| 98042         | 4-NONENE                     |                |
| 98043         | ISOPROPYLBENZENE (CUMENE)    | 0.0075         |
| 98045         | M-DIETHYLBENZENE             | 0.0202         |
| 98046         | NAPHTHALENE                  | 0.0272         |
| 98047         | ISOBUTYLBENZENE              |                |
| 98048         | INDENE                       | 0.0011         |
| 98049         | C9 AROMATICS                 | 0.0001         |
| 98050         | C10 AROMATICS                | 0.0211         |
| 98051         | 2-CHLOROTOLUENE              |                |
| 98052         | T-BUTYLBENZENE               |                |
| 98055         | 2,4,4-TRIMETHYL-2-PENTENE    |                |
| 98061         | ETHYLCYCLOHEXANE             | 0.0036         |
| 98064         | C2 CYCLOHEXANE               | 0.0152         |
| 98065         | C3 CYCLOHEXANE               |                |
| 98066         | C4 CYCLOHEXANE               |                |
| 98067         | C5 CYCLOHEXANE               |                |
| 98068         | C3 ALKYL CYCLOHEXANE         | 0.0433         |
| 98069         | C4 ALKYL CYCLOHEXANE         | 0.0226         |
| 98070         | C4 SUBSTITUTED CYCLOHEXANE   |                |
| 98071         | C5 SUBSTITUTED CYCLOHEXANE   | 0.0158         |
| 98072         | C6 SUBSTITUTED CYCLOHEXANE   | 0.0118         |
| 98073         | C4 SUBSTITUTED CYCLOHEXANONE | 0.0090         |
| 98074         | BUTYL CELLOSOLVE             | 0.0173         |
| 98075         | C5 ESTER                     | 0.0050         |
| 98076         | 2-METHYL-3-HEXANONE          | 0.0148         |
| 98077         | HEPTANONE                    | 0.0033         |
| 98078         | ALKENE KETONE                |                |
| 98079         | TERPINENE                    |                |
| 98084         | C2 ALKYL INDAN               | 0.0426         |

(continued)

Table 15 (continued) - 3

| SAROAD<br>No. | Description                   | Weight Percent |
|---------------|-------------------------------|----------------|
| 98085         | ALKYL SUBSTITUTED CYCLOHEXANE |                |
| 98086         | C2 ALKYL DECALIN              | 0.0149         |
| 98087         | CARVOMENTHOL                  |                |
| 98088         | CARVONE                       |                |
| 98089         | ISOPULEGONE                   |                |
| 98093         | C7 ESTER                      |                |
| 98094         | PENTYL ALCOHOL                |                |
| 98095         | C6 ALDEHYDE                   |                |
| 98096         | CARBITOL                      |                |
| 98097         | A-TERPINEOL                   |                |
| 98098         | PARAFFIN BOND                 | 4.5481         |
| 98099         | OLEFIN BOND                   | 0.0480         |
| 98100         | ETHYLENE BOND                 | 0.2415         |
| 98101         | CARBONYL BOND                 |                |
| 98102         | AROMATIC BOND                 |                |
| 98103         | UNREACTIVE BOND               | 2.0284         |
| 98104         | 1-CHLOROBUTANE                | 0.0110         |
| 98105         | 3-(CHLOROMETHYL)-HEPTANE      | 0.0031         |
| 98107         | DIBUTYL ETHER                 | 0.0012         |
| 98108         | 2-BUTYLtetrahydrofuran        | 0.0007         |
| 98109         | PROPYLCYCLOHEXANONE           | 0.0052         |
| 98110         | 2-(2-BUTOXYETHOXY)-ETHANOL    | 0.0039         |
| 98111         | 1-ETHOXY-2-PROPANOL           | 0.0073         |
| 98112         | 2-ETHYL-1-HEXANOL             | 0.0050         |
| 98113         | 1-HEPTANOL                    | 0.0039         |
| 98114         | METHYL ISOBUTYRATE            | 0.0006         |
| 98115         | ISOAMYL ISOBUTYRATE           | 0.0018         |
| 98116         | SUBSTITUTED C7 ESTER (C12)    | 0.1346         |
| 98117         | SUBSTITUTED C9 ESTER (C12)    | 0.1426         |
| 98118         | METHYL ACRYLATE               | 0.0001         |
| 98119         | VINYL ACETATE                 | 0.0000         |
| 98120         | METHACRYLONITRILE             |                |
| 99001         | ALLYL CHLORIDE                |                |
| 99002         | BENZYL CHLORIDE               |                |
| 99003         | CHLOROPRENE                   |                |
| 99006         | EPICHLOROHYDRIN               |                |
| 99007         | HEXACHLOROCYCLOPENTADIENE     |                |
| 99008         | MALEIC ANHYDRIDE              |                |
| 99009         | NITROBENZENE                  |                |
| 99010         | NITROSOMORPHOLINE             |                |
| 99013         | 1,1-DICHLOROETHENE            |                |
| 99014         | ETHYLENE DIBROMIDE            | 0.0000         |
| 99015         | DIBENZOFURAN                  |                |
| 99016         | 1,2-DICHLOROPROPANE           |                |
| 99017         | BROMODICHLOROMETHANE          |                |

(continued)

Table 15 (continued) - 4

| SAROAD<br>No. | Description              | Weight Percent |
|---------------|--------------------------|----------------|
| 99018         | TRANS-1,2-DICHLOROETHENE |                |
| 99019         | BROMOFORM                |                |
| 99020         | CHLORODIBROMOMETHANE     |                |
| 99021         | 3-CARENE                 | 0.0048         |
| 99024         | M & P-XYLENE             |                |
| 99902         | FURAN                    |                |
| 99903         | GLYOXAL                  |                |

Table 16. Emissions Categories for which there are Inconsistencies in Chemical Identification between the 1983 California Emissions Data Base and the EPA/NAPAP Emissions Inventory, and Weight Percents of Emissions of these Categories into California or the Contiguous United States for the Respective Inventories

| No.   | Description  | Weight Percent<br>USA | Weight Percent<br>Calif. |
|-------|--|-----------------------|--------------------------|
| 43111 | NAPAP = ISOMERS OF DODECANE<br>CALIF = ISOMERS OF TRIDECANE  | 0.0431                | 0.0364                   |
| 43112 | NAPAP = ISOMERS OF TRIDECANE<br>CALIF = ISOMERS OF DODECANE  | 0.0004                | 0.0146                   |
| 43227 | NAPAP = <u>CIS</u> -2-PENTENE<br>CALIF = 2- AND 3-PENTENES   | 0.1649                | 0.0370                   |
| 43264 | NAPAP = HEPTENE<br>CALIF = CYCLOHEXANONE                     | 0.0129                |                          |
| 43269 | NAPAP = 1-NONENE<br>CALIF = 1-UNDECENE                       | 0.0023                | 0.0056                   |
| 43271 | NAPAP = 3,5,5-TRIMETHYLHEXANE<br>CALIF = 2,4-DIMETHYLPENTANE | 0.0011                | 0.0599                   |
| 43275 | NAPAP = 2-METHYL-1,3-BUTADIENE<br>CALIF = 2-METHYLHEXANE     | 0.0272                |                          |
| 43276 | NAPAP = 2,3 DIMETHYLBUTANE<br>CALIF = 2,2,4-TRIMETHYLPENTANE | 0.2677                | 0.1776                   |
| 43281 | NAPAP = 1-BUTYNE<br>CALIF = N-HEXADECANE                     | 0.0558                |                          |
| 43282 | NAPAP = 2-BUTYNE<br>CALIF = N-HEPTADECANE                    | 0.0395                |                          |
| 43283 | NAPAP = C-3-HEXENE<br>CALIF = N-OCTADECANE                   | 0.0328                |                          |
| 43284 | NAPAP = 2-METHYL-2-PENTENE<br>CALIF = N-NONADECAN            | 0.1803                |                          |
| 43285 | NAPAP = 2-HEXENE<br>CALIF = N-EICOSANE                       | 0.0816                |                          |
| 43286 | NAPAP = DIMETHYLHEXENE<br>CALIF = N-HENEICOSANE              | 0.0552                |                          |

(continued)

Table 16 (continued) - 2

| No.   | Description   | Weight Percent<br>USA | Weight Percent<br>Calif. |
|-------|---|-----------------------|--------------------------|
| 43287 | NAPAP = 2,2 DIMETHYLHEXANE<br>CALIF = N-DOCOSANE                        | 0.0245                |                          |
| 43296 | NAPAP = 2-METHYLHEPTANE<br>CALIF = 2,2,3-TRIMETHYLPENTANE               | 0.0735                |                          |
| 43312 | NAPAP = 2-(2-BUTOXYETHOXY)-ETHANOL<br>CALIF = 1-T-2-C-4-TM-CYCLOPENTANE | 0.0001                |                          |
| 43513 | NAPAP = GLYOXAL<br>CALIF = C8 ALDEHYDE                                  | 0.0218                | 0.1075                   |
| 43561 | NAPAP = CYCLOHEXANONE<br>CALIF = METHYL AMYL KETONE                     | 0.0043                |                          |
| 43819 | NAPAP = METHYLENE BROMIDE<br>CALIF = METHYL BROMIDE                     | 0.0115                |                          |
| 45232 | NAPAP = DIPHENYL ETHANE<br>CALIF = TETRAMETHYLBENZENE                   | 0.0073                |                          |
| 45233 | NAPAP = ETHYL-PHENYL-PHENYL-ETHANE<br>CALIF = TRI/TETRAALKYL BENZENE    | 0.0007                | 0.0419                   |
| 46201 | NAPAP = DIHYDROXYNAPTHALENEDIONE<br>CALIF = 1,4-DIOXANE                 | 0.0004                |                          |
| 98024 | NAPAP = (NO LABEL)<br>CALIF = BENZYL CHLORIDE                           | 0.0015                |                          |
| 98037 | NAPAP = 1-METHYLCYCLOHEXENE<br>CALIF = 1-METHYLCYCLOHEXANE              | 0.0005                | 0.0166                   |
| 98080 | NAPAP = (NO LABEL)<br>CALIF = BUTANDIOL                                 | 0.0002                | 0.0247                   |
| 43511 | NAPAP = ISOBUTYRALDEHYDE<br>CALIF = C3 ALDEHYDE                         | 0.0016                |                          |
| 45108 | NAPAP = ISOMERS OF PROPYLBENZENE<br>CALIF = PROPYLBENZENE               | 0.0783                |                          |
| 45300 | NAPAP = PHENOL<br>CALIF = PHENOLS                                       | 0.1149                | 0.0000                   |

Assignments of detailed model species, OH radial rate constants, and molecular weights were then made for approximately 350 of the most important (in terms of mass emissions given in Tables 13-16) of these SAROAD categories. Assignments were made for essentially all of the SAROAD classes which had nonzero emissions in the 1983 California inventory, and for classes accounting for over 94% of the identified United States emissions in the EPA/NAPAP inventory. The resulting assignments are given in Table 17. That table also gives notes indicating our assessment of the degree of uncertainty in the chemical mechanism used for the model species, the type of representation used, and, for emissions categories representing mixtures of compounds, uncertainties in the characterization of the composition or reactivity of the mixture. The table also gives footnotes describing special estimates which had to be made for some of the emissions categories. The data given in Table 17 were derived from computer data sets which are part of the emissions processing system which was developed for this program (Carter 1988).

As indicated by the footnotes to Table 17, there were a number of SAROAD categories which we believe to be poorly characterized as to their chemical composition or atmospheric reactivity, and for which assignments of model species was difficult or uncertain. The worst example is the fact that a number of California air basins have significant emissions of SAROAD classes which correspond not to real chemicals, but to lumped structure groups used in the Carbon Bond mechanism. While we attempted to assign detailed model species to those classes, we do not consider these assignments very reliable, and we recommend that emissions profiles containing significant emissions of these classes not be used in airshed model simulations employing mechanisms other than the particular version of the Carbon Bond mechanism which was employed when these classes were derived. Fortunately, those categories are not used in the EPA/NAPAP data base. On the other hand, both data bases include non-negligible emissions of categories called "NAPHTHA," "MINERAL SPIRITS," or "LACTOL SPIRITS" which refer to mixtures whose compositions are not characterized. In those cases, we made an estimate of their composition based on an analysis of mineral spirits; but this should be considered to be uncertain. The largest number of classes which we consider to be poorly characterized are those referring to isomeric mixtures of alkenes. These classes are

Table 17. Assignments of Detailed Model Species, OH Radical Rate Constants, and Molecular Weights to the Major SAROAD Emissions Classes used in the California and EPA/NAPAP Data Bases

| ID    | SET <sup>a</sup><br>NO. | Description            | Factor <sup>b</sup> | Model<br>Species | kOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech Mix | Notes <sup>e</sup> |
|-------|-------------------------|------------------------|---------------------|------------------|------------------|------------------|--------------------------------|--------------------|
| 42101 |                         | CO                     | 1.0000              | CO               | 3.52E+02         | 28.01            | 1                              | 1                  |
| 43105 |                         | ISOMERS OF HEXANE      | 1.0000              | BR-C6            | 7.93E+03         | 86.17            | 2                              | 2                  |
| 43106 |                         | ISOMERS OF HEPTANE     | 1.0000              | BR-C7            | 1.05E+04         | 100.20           | 2                              | 2                  |
| 43107 |                         | ISOMERS OF OCTANE      | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                              | 2                  |
| 43108 |                         | ISOMERS OF NONANE      | 1.0000              | BR-C9            | 1.54E+04         | 128.25           | 2                              | 2                  |
| 43109 |                         | ISOMERS OF DECANE      | 1.0000              | BR-C10           | 1.75E+04         | 142.28           | 2                              | 2                  |
| 43110 |                         | ISOMERS OF UNDECANE    | 1.0000              | BR-C11           | 2.10E+04         | 156.30           | 2                              | 2                  |
| 43111 | E                       | ISOMERS OF DODECANE    | 1.0000              | BR-C12           | 2.30E+04         | 170.33           | 2                              | 2                  |
| 43111 | A                       | ISOMERS OF TRIDECANE   | 1.0000              | BR-C13           | 2.51E+04         | 184.36           | 2                              | 2                  |
| 43112 | E                       | ISOMERS OF TRIDECAINE  | 1.0000              | BR-C13           | 2.51E+04         | 184.36           | 2                              | 2                  |
| 43112 | A                       | ISOMERS OF DODECANE    | 1.0000              | BR-C12           | 2.30E+04         | 170.33           | 2                              | 2                  |
| 43113 |                         | ISOMERS OF TETRADECANE | 1.0000              | BR-C14           | 2.71E+04         | 198.38           | 2                              | 2                  |
| 43114 |                         | ISOMERS OF PENTADECANE | 1.0000              | BR-C15           | 2.92E+04         | 212.41           | 2                              | 2                  |
| 43115 | C-7                     | CYCLOPARAFFINS         | 1.0000              | CYC-C7           | 1.50E+04         | 98.19            | 2                              | 2                  |
| 43116 | C-8                     | CYCLOPARAFFINS         | 1.0000              | CYC-C8           | 1.79E+04         | 112.23           | 2                              | 2                  |
| 43117 | C-9                     | CYCLOPARAFFINS         | 1.0000              | CYC-C9           | 2.05E+04         | 126.26           | 2                              | 2                  |
| 43118 |                         | MINERAL SPIRITS.       | 0.0066              | N-C8             | 1.20E+04         | 114.23           | 2                              | 5                  |
|       |                         |                        | 0.0803              | N-C9             | 1.40E+04         | 128.26           |                                |                    |
|       |                         |                        | 0.1141              | N-C10            | 1.61E+04         | 142.29           |                                |                    |
|       |                         |                        | 0.0873              | N-C11            | 1.82E+04         | 156.31           |                                |                    |
|       |                         |                        | 0.0268              | N-C12            | 2.02E+04         | 170.34           |                                |                    |
|       |                         |                        | 0.0030              | BR-C8            | 1.26E+04         | 114.23           |                                |                    |
|       |                         |                        | 0.0358              | BR-C9            | 1.54E+04         | 128.26           |                                |                    |
|       |                         |                        | 0.0509              | BR-C10           | 1.75E+04         | 142.29           |                                |                    |
|       |                         |                        | 0.0388              | BR-C11           | 2.10E+04         | 156.31           |                                |                    |
|       |                         |                        | 0.0119              | BR-C12           | 2.30E+04         | 170.34           |                                |                    |
|       |                         |                        | 0.1008              | CYC-C9           | 2.05E+04         | 126.24           |                                |                    |
|       |                         |                        | 0.2503              | CYC-C10          | 2.34E+04         | 140.27           |                                |                    |
|       |                         |                        | 0.1007              | CYC-C11          | 2.60E+04         | 154.30           |                                |                    |
|       |                         |                        | 0.0185              | CYC-C12          | 2.89E+04         | 168.32           |                                |                    |
|       |                         |                        | 0.0630              | M-XYLENE         | 3.59E+04         | 106.17           |                                |                    |
|       |                         |                        | 0.0031              | NAPHTHAL         | 3.11E+04         | 128.17           |                                |                    |

(continued)

Table 17 (continued) - 2

| ID    | SET <sup>a</sup><br>NO. | Description        | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|--------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 43119 |                         | LACTOL SPIRITS     |                     |                  |                  |                  |                            |                           |
|       | 0.0010                  | ME-NAPH            | 7.63E+04            | 142.20           |                  |                  |                            |                           |
|       | 0.0071                  | TETRALIN           | 5.03E+04            | 132.21           |                  |                  |                            |                           |
|       | 0.0066                  | N-C8               | 1.20E+04            | 114.23           | 2                |                  |                            |                           |
|       | 0.0803                  | N-C9               | 1.40E+04            | 128.26           |                  |                  |                            |                           |
|       | 0.1141                  | N-C10              | 1.61E+04            | 142.29           |                  |                  |                            |                           |
|       | 0.0873                  | N-C11              | 1.82E+04            | 156.31           |                  |                  |                            |                           |
|       | 0.0268                  | N-C12              | 2.02E+04            | 170.34           |                  |                  |                            |                           |
|       | 0.0030                  | BR-C8              | 1.26E+04            | 114.23           |                  |                  |                            |                           |
|       | 0.0358                  | BR-C9              | 1.54E+04            | 128.26           |                  |                  |                            |                           |
|       | 0.0509                  | BR-C10             | 1.75E+04            | 142.29           |                  |                  |                            |                           |
|       | 0.0388                  | BR-C11             | 2.10E+04            | 156.31           |                  |                  |                            |                           |
|       | 0.0119                  | BR-C12             | 2.30E+04            | 170.34           |                  |                  |                            |                           |
|       | 0.1008                  | CYC-C9             | 2.05E+04            | 126.24           |                  |                  |                            |                           |
|       | 0.2503                  | CYC-C10            | 2.34E+04            | 140.27           |                  |                  |                            |                           |
|       | 0.1007                  | CYC-C11            | 2.60E+04            | 154.30           |                  |                  |                            |                           |
|       | 0.0185                  | CYC-C12            | 2.89E+04            | 168.32           |                  |                  |                            |                           |
|       | 0.0630                  | M-XYLENE           | 3.59E+04            | 106.17           |                  |                  |                            |                           |
|       | 0.0031                  | NAPHTHAL           | 3.11E+04            | 128.17           |                  |                  |                            |                           |
|       | 0.0010                  | ME-NAPH            | 7.63E+04            | 142.20           |                  |                  |                            |                           |
|       | 0.0071                  | TETRALIN           | 5.03E+04            | 132.21           |                  |                  |                            |                           |
|       | 0.2500                  | 1-BUTENE           | 4.56E+04            | 56.10            | 1                | 4                |                            |                           |
|       | 0.2500                  | ISOBUTEN           | 7.47E+04            | 56.10            |                  |                  |                            |                           |
|       | 0.2500                  | C-2-BUTE           | 8.14E+04            | 56.10            |                  |                  |                            |                           |
|       | 0.2500                  | T-2-BUTE           | 9.24E+04            | 56.10            |                  |                  |                            |                           |
|       | 0.5000                  | C5-OLE1            | 4.56E+04            | 70.13            | 2                | 4                |                            |                           |
|       | 0.5000                  | C5-OLE2            | 9.24E+04            | 70.13            |                  |                  |                            |                           |
|       | 1.0000                  | BR-C5              | 5.87E+03            | 72.15            | 1                | 2                |                            |                           |
|       | 0.5000                  | A-PINENE           | 7.73E+04            | 136.24           | 3                | 4                |                            |                           |
|       | 0.5000                  | B-PINENE           | 1.14E+05            | 136.24           |                  |                  |                            |                           |
|       | 0.5000                  | C10-OLE1           | 5.37E+04            | 140.27           | 2                | 4                |                            |                           |
|       | 0.5000                  | C10-OLE2           | 9.24E+04            | 140.27           |                  |                  |                            |                           |
|       | 1.0000                  | CYC-C8             | 1.79E+04            | 112.22           | 2                | 2                |                            |                           |
|       | 1.0000                  | CYC-C9             | 2.05E+04            | 126.24           | 2                | 2                |                            |                           |
| 43120 |                         | ISOMERS OF BUTENE  |                     |                  |                  |                  |                            |                           |
| 43121 |                         | ISOMERS OF PENTENE |                     |                  |                  |                  |                            |                           |
| 43122 |                         | ISOMERS OF PENTANE |                     |                  |                  |                  |                            |                           |
| 43123 |                         | TERPENES           |                     |                  |                  |                  |                            |                           |
| 43125 |                         | C10 OLEFINS        |                     |                  |                  |                  |                            |                           |
| 43126 | C2                      | CYCLOHEXANE        |                     |                  |                  |                  |                            |                           |
| 43127 | C3                      | CYCLOHEXANE        |                     |                  |                  |                  |                            |                           |

(continued)

Table 17 (continued) - 3

| ID    | SET <sup>a</sup><br>NO. | Description                | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|----------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 43129 |                         | C4 SUBSTITUTED CYCLOHEXANE | 1.0000              | CYC-C10          | 2.34E+04         | 140.27           | 2                          | 2                         |
| 43135 |                         | C10 PARAFFIN               | 1.0000              | BR-C10           | 1.75E+04         | 142.28           | 2                          | 2                         |
| 43141 |                         | C8 PARAFFIN                | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 2                         |
| 43143 |                         | C5 OLEFIN                  | 0.5000              | C5-OLE1          | 4.56E+04         | 70.13            | 2                          | 4                         |
| 43144 |                         | C5 PARAFFIN                | 0.5000              | C5-OLE2          | 9.24E+04         | 70.13            | 1                          | 2                         |
| 43150 | C10H18                  | METHANE                    | 1.0000              | BR-C5            | 5.87E+03         | 72.15            | 1                          | 2                         |
| 43201 |                         | ETHANE                     | 1.0000              | BR-C10           | 1.75E+04         | 142.28           | 2                          | 4                         |
| 43202 |                         | ETHYLENE                   | 1.0000              | METHANE          | 1.29E+01         | 16.04            | 1                          | 1                         |
| 43203 |                         | PROPANE                    | 1.0000              | ETHANE           | 4.12E+02         | 30.07            | 1                          | 1                         |
| 43204 |                         | PROPYLENE                  | 1.0000              | ETHENE           | 1.24E+04         | 28.05            | 1                          | 1                         |
| 43205 |                         | ACETYLENE                  | 1.0000              | PROPANE          | 1.80E+03         | 44.09            | 1                          | 1                         |
| 43206 |                         | CYCLOPROPANE               | 1.0000              | PROPENE          | 3.82E+04         | 42.08            | 1                          | 1                         |
| 43207 |                         | METHYLACETYLENE            | 1.0000              | ACETYLEN         | 1.15E+03         | 26.04            | 3                          | 0                         |
| 43209 |                         | 3-METHYL-1-PENTENE         | 1.0000              | CYC-C3           | 0.00E-01         | 42.08            | 3                          | 1                         |
| 43211 |                         | N-BUTANE                   | 1.0000              | ME-ACTYL         | 8.90E+03         | 40.06            | 4                          | 1                         |
| 43212 |                         | 1-BUTENE                   | 1.0000              | C6-OLE1          | 5.37E+04         | 84.16            | 2                          | 2                         |
| 43213 |                         | ISO-BUTANE                 | 1.0000              | N-C4             | 3.75E+03         | 58.12            | 1                          | 1                         |
| 43214 |                         | ISOBUTYLENE                | 1.0000              | 1-BUTENE         | 4.56E+04         | 56.10            | 1                          | 1                         |
| 43215 |                         | TRANS-2-BUTENE             | 1.0000              | ISO-C4           | 3.50E+03         | 58.12            | 1                          | 1                         |
| 43216 |                         | CIS-2-BUTENE               | 1.0000              | ISOBUTEN         | 7.47E+04         | 56.10            | 1                          | 1                         |
| 43217 |                         | 1,3-BUTADIENE              | 1.0000              | T-2-BUTE         | 9.24E+04         | 56.10            | 1                          | 1                         |
| 43218 |                         | ETHYLACETYLENE             | 1.0000              | T-2-BUTE         | 9.24E+04         | 56.10            | 1                          | 1                         |
| 43219 |                         | N-PENTANE                  | 1.0000              | 13-BUTDE         | 9.71E+04         | 54.09            | 3                          | 1                         |
| 43220 |                         | ISO PENTANE                | 1.0000              | ET-ACTYL         | 4.56E+04         | 54.09            | 4                          | 1                         |
| 43221 |                         | 3-METHYL-1-BUTENE          | 1.0000              | N-C5             | 5.87E+03         | 72.15            | 1                          | 1                         |
| 43223 |                         | 1-PENTENE                  | 1.0000              | 3M-1-BUT         | 4.61E+04         | 70.13            | 2                          | 1                         |
| 43224 |                         | 2-METHYL-1-BUTENE          | 1.0000              | 1-PENTEN         | 4.56E+04         | 70.13            | 2                          | 1                         |
| 43225 |                         | TRANS-2-PENTENE            | 1.0000              | 2M-1-BUT         | 8.80E+04         | 70.13            | 2                          | 1                         |
| 43226 |                         | E CIS-2-PENTENE            | 1.0000              | C5-OLE2          | 9.24E+04         | 70.13            | 2                          | 2                         |
| 43227 | E                       | 2- AND 3-PENTENES          | 1.0000              | C5-OLE2          | 9.24E+04         | 70.13            | 2                          | 2                         |
| 43228 | A                       | 2-METHYL-2-BUTENE          | 1.0000              | 2M-2-BUT         | 1.26E+05         | 70.13            | 2                          | 1                         |

(continued)

Table 17 (continued) - 4

| ID    | SET <sup>a</sup><br>NO. | Description            | Factor <sup>b</sup> | Model<br>Species | kOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Mix | Notes <sup>e</sup> |
|-------|-------------------------|------------------------|---------------------|------------------|------------------|------------------|----------------------------|-----|--------------------|
| 43229 |                         | 2-METHYL PENTANE       | 1.0000              | BR-C6            | 7.93E+03         | 86.17            | 1                          | 2   |                    |
| 43230 |                         | 3-METHYL PENTANE       | 1.0000              | BR-C6            | 7.93E+03         | 86.17            | 1                          | 2   |                    |
| 43231 |                         | N-HEXANE               | 1.0000              | N-C6             | 7.87E+03         | 86.17            | 1                          | 1   |                    |
| 43232 |                         | N-HEPTANE              | 1.0000              | N-C7             | 9.92E+03         | 100.20           | 2                          | 1   |                    |
| 43233 |                         | N-OCTANE               | 1.0000              | N-C8             | 1.20E+04         | 114.23           | 2                          | 1   |                    |
| 43234 |                         | 2,3-DIMETHYL-1-BUTENE  | 1.0000              | C6-OLE1          | 5.37E+04         | 84.16            | 2                          | 2   |                    |
| 43235 |                         | N-NONANE               | 1.0000              | N-C9             | 1.40E+04         | 128.25           | 2                          | 1   |                    |
| 43238 |                         | N-DECANE               | 1.0000              | N-C10            | 1.61E+04         | 142.28           | 2                          | 1   |                    |
| 43241 |                         | N-UNDECANE             | 1.0000              | N-C11            | 1.82E+04         | 156.30           | 2                          | 1   |                    |
| 43242 |                         | CYCLOPENTANE           | 1.0000              | CYCC5            | 8.24E+03         | 70.14            | 2                          | 1   |                    |
| 43243 |                         | ISOPRENE               | 1.0000              | ISOPRENE         | 1.46E+05         | 68.11            | 3                          | 1   |                    |
| 43245 |                         | 1-HEXENE               | 1.0000              | 1-HEXENE         | 5.37E+04         | 84.16            | 2                          | 1   |                    |
| 43247 |                         | 2,4-DIMETHYLPENTANE    | 1.0000              | BR-C7            | 1.05E+04         | 100.20           | 2                          | 2   |                    |
| 43248 |                         | CYCLOHEXANE            | 1.0000              | CYC-C6           | 1.23E+04         | 84.16            | 2                          | 1   |                    |
| 43250 |                         | 2,2,4-TRIMETHYLPENTANE | 1.0000              | ISO-C8           | 6.88E+03         | 114.23           | 2                          | 1   |                    |
| 43252 |                         | 2,3,4-TRIMETHYLPENTANE | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 2   |                    |
| 43255 |                         | N-DODECANE             | 1.0000              | N-C12            | 2.02E+04         | 170.33           | 2                          | 1   |                    |
| 43256 |                         | A-PINENE               | 1.0000              | A-PINENE         | 7.73E+04         | 136.24           | 3                          | 2   |                    |
| 43258 |                         | N-TRIDECANE            | 1.0000              | N-C13            | 2.23E+04         | 184.36           | 2                          | 1   |                    |
| 43259 |                         | N-TETRADECANE          | 1.0000              | N-C14            | 2.43E+04         | 198.38           | 2                          | 1   |                    |
| 43260 |                         | N-PENTADECANE          | 1.0000              | N-C15            | 2.64E+04         | 212.41           | 2                          | 1   |                    |
| 43261 |                         | METHYLCYCLOHEXANE      | 1.0000              | ME-CYCC6         | 1.50E+04         | 98.19            | 2                          | 1   |                    |
| 43262 |                         | METHYLCYCLOPENTANE     | 1.0000              | ME-CYCC5         | 1.04E+04         | 84.16            | 2                          | 1   |                    |
| 43264 | E                       | HEPTENE                | 1.0000              | C7-OLE1          | 5.37E+04         | 98.18            | 2                          | 2   |                    |
| 43264 | A                       | CYCLOHEXANONE          | 1.0000              | MEK              | 1.92E+03         | 98.15            | 4                          | 2   |                    |
| 43265 |                         | OCTENE                 | 1.0000              | C8-OLE1          | 5.37E+04         | 112.21           | 2                          | 4   |                    |
| 43266 |                         | C-2-OCTENE             | 1.0000              | C8-OLE2          | 9.24E+04         | 112.21           | 2                          | 2   |                    |
| 43267 |                         | 1-NONENE               | 1.0000              | C9-OLE1          | 5.37E+04         | 126.24           | 2                          | 2   |                    |
| 43268 |                         | 1-DECENE               | 1.0000              | C10-OLE1         | 5.37E+04         | 140.27           | 2                          | 2   |                    |
| 43269 | E                       | 1-NONENE               | 1.0000              | C9-OLE1          | 5.37E+04         | 126.24           | 2                          | 2   |                    |
| 43269 | A                       | 1-UNDECENE             | 1.0000              | C11-OLE1         | 5.37E+04         | 154.30           | 2                          | 2   |                    |
| 43270 |                         | 3-METHYL-1-2-PENTENE   | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 2   |                    |
| 43271 | E                       | 3,5,5-TRIMETHYLPENTANE | 1.0000              | BR-C9            | 1.54E+04         | 128.26           | 2                          | 2   |                    |

(continued)

Table 17 (continued) - 5

| ID    | SET <sup>a</sup><br>NO. | Description            | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 43271 | A                       | 2,4-DIMETHYLPENTANE    | 1.0000              | BR-C7            | 1.05E+04         | 100.20           | 2                          | 2                         |
| 43272 |                         | METHYLCYCLOPENTENE     | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 1                         |
| 43273 |                         | CYCLOHEXENE            | 1.0000              | CYC-HEXE         | 9.82E+04         | 84.16            | 3                          | 1                         |
| 43274 |                         | 2,3-DIMETHYLPENTANE    | 1.0000              | BR-C7            | 1.05E+04         | 100.20           | 2                          | 2                         |
| 43275 | E                       | 2-METHYL-1,3-BUTADIENE | 1.0000              | ISOPRENE         | 1.46E+05         | 68.11            | 3                          | 1                         |
| 43275 | A                       | 2-METHYLHEXANE         | 1.0000              | BR-C7            | 1.05E+04         | 100.20           | 2                          | 2                         |
| 43276 | E                       | 2,3-DIMETHYLBUTANE     | 1.0000              | 23-DMB           | 7.99E+03         | 86.17            | 2                          | 2                         |
| 43276 | A                       | 2,2,4-TRIMETHYLPENTANE | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 2                         |
| 43277 |                         | 2,4-DIMETHYLHEXANE     | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 2                         |
| 43278 |                         | 2,5-DIMETHYLHEXANE     | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 2                         |
| 43279 |                         | 2,3,4-TRIMETHYLPENTANE | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 2                         |
| 43280 |                         | 2,3,3-TRIMETHYLPENTANE | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 2                         |
| 43281 | A                       | N-HEXADECANE           | 1.0000              | N-C16            | 2.64E+04         | 226.44           | 2                          | 1                         |
| 43282 | A                       | N-HEPTADECANE          | 1.0000              | N-C17            | 2.64E+04         | 240.46           | 2                          | 1                         |
| 43283 | E                       | C-3-HEXENE             | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 1                         |
| 43283 | A                       | N-OCTADECANE           | 1.0000              | N-C18            | 2.64E+04         | 254.49           | 2                          | 1                         |
| 43284 | E                       | 2-METHYL-2-PENTENE     | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 1                         |
| 43284 | A                       | N-NONADECANE           | 1.0000              | N-C19            | 2.64E+04         | 268.51           | 2                          | 1                         |
| 43285 | E                       | 2-HEXENE               | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 1                         |
| 43285 | A                       | N-EICOSANE             | 1.0000              | N-C20            | 2.64E+04         | 282.54           | 2                          | 1                         |
| 43286 | E                       | DIMETHYLHEXENE         | 0.5000              | C8-OLE1          | 5.37E+04         | 112.23           | 2                          | 4                         |
| 43286 |                         |                        | 0.5000              | C8-OLE2          | 9.24E+04         | 112.23           |                            |                           |
| 43286 |                         |                        | 0.5000              | N-C21            | 2.64E+04         | 296.57           | 2                          | 1                         |
| 43287 | E                       | 2,2-DIMETHYLHEXANE     | 1.0000              | BR-C8            | 1.26E+04         | 114.22           | 2                          | 1                         |
| 43287 | A                       | N-DOCOSANE             | 1.0000              | N-C22            | 2.64E+04         | 310.59           | 2                          | 1                         |
| 43288 |                         | ETHYLCYCLOHEXANE       | 1.0000              | CYC-C8           | 1.79E+04         | 112.23           | 2                          | 2                         |
| 43289 | C6                      | OLEFINS                | 0.5000              | C6-OLE1          | 5.37E+04         | 84.16            | 2                          | 4                         |
| 43290 | C8                      | OLEFINS                | 0.5000              | C8-OLE1          | 5.37E+04         | 112.23           | 2                          | 4                         |
| 43291 |                         | 2,2-DIMETHYLBUTANE     | 1.0000              | 22-DMB           | 2.71E+03         | 86.17            | 1                          | 1                         |
| 43292 |                         | CYCLOPENTENE           | 1.0000              | CYC-PNTE         | 9.74E+04         | 70.14            | 2                          | 1                         |
| 43293 |                         | 4-METHYL-T-2-PENTENE   | 1.0000              | C6-OLE2          | 9.24E+04         | 84.16            | 2                          | 2                         |

(continued)

Table 17 (continued) - 6

| ID    | SET <sup>a</sup><br>NO. | Description                | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|----------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 43294 |                         | C7-OLEFINS                 | 0.5000              | C7-OLE1          | 5.37E+04         | 98.18            | 2                          | 4 2                       |
|       |                         | 3-METHYLHEXANE             | 0.5000              | C7-OLE2          | 9.24E+04         | 98.18            | 100.20                     | 2 2                       |
| 43295 | E                       | 2-METHYLHEPTANE            | 1.0000              | BR-C7            | 1.05E+04         | 114.23           | 2                          | 2                         |
| 43296 | A                       | 2,2,3-TRIMETHYLPENTANE     | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 2                         |
| 43296 | A                       | 4-METHYLHEPTANE            | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 2                         |
| 43297 |                         | 3-METHYLHEPTANE            | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 2                         |
| 43298 |                         | 2,2,5-TRIMETHYLPENTANE     | 1.0000              | BR-C8            | 1.26E+04         | 114.23           | 2                          | 0                         |
| 43299 |                         | METHYL ALCOHOL             | 1.0000              | MEOH             | 1.34E+03         | 32.04            | 1                          | 1                         |
| 43301 |                         | ETHYL ALCOHOL              | 1.0000              | ETOH             | 4.30E+03         | 46.07            | 1                          | 1                         |
| 43302 |                         | N-PROPYL ALCOHOL           | 1.0000              | N-C3-OH          | 7.78E+03         | 60.09            | 1                          | 1                         |
| 43303 |                         | ISO-PROPYL ALCOHOL         | 1.0000              | I-C3-OH          | 9.10E+03         | 60.09            | 1                          | 1                         |
| 43304 |                         | N-BUTYL ALCOHOL            | 1.0000              | N-C4-OH          | 9.37E+03         | 74.12            | 1                          | 1                         |
| 43305 |                         | ISO-BUTYL ALCOHOL          | 1.0000              | I-C4-OH          | 1.40E+04         | 74.12            | 1                          | 1                         |
| 43306 |                         | 2-BUTOXY-ETHANOL           | 0.1900              | RCHO-H           | 1.96E-11         | 118.17           | 3                          | 2 3                       |
| 43308 |                         | TERT-BUTYL ALCOHOL         | 0.8100              | [N-C6]           | 1.96E-11         | 118.17           |                            |                           |
|       |                         | 2-METHOXYETHANOL           | 1.0000              | T-C4-OH          | 1.60E+03         | 74.12            | 1                          | 1                         |
| 43309 |                         | 2-ETHOXYETHANOL            | 0.3500              | RCHO-H           | 1.12E-11         | 76.09            | 3                          | 1                         |
| 43310 |                         |                            | 0.6500              | A1A3-R           | 1.12E-11         | 76.09            |                            |                           |
|       |                         |                            | 0.2500              | RCHO-H           | 1.56E-11         | 90.12            | 3                          | 1                         |
| 43311 |                         |                            | 0.4000              | A1A3-R           | 1.56E-11         | 90.12            |                            |                           |
|       |                         |                            | 0.3500              | RCHO-H           | 1.56E-11         | 90.12            |                            |                           |
|       |                         |                            | 0.1000              | RCHO-H           | 3.28E-11         | 162.18           | 3                          | 2 6                       |
|       |                         |                            | 0.9000              | [N-C8]           | 3.28E-11         | 162.18           |                            |                           |
| 43312 | E                       | 2-(2-BUTOXYETHOXY)-ETHANOL | 1.0000              | CYC-C8           | 1.79E+04         | 112.23           | 2                          | 2                         |
|       |                         |                            | 1.0000              | ME-O-ME          | 4.42E+03         | 46.07            | 2                          | 1                         |
|       |                         |                            | 1.0000              | [N-C4]           | 1.34E-11         | 74.12            | 3                          | 2                         |
| 43312 | A                       | 1-T-2-C-4-TM-CYCLOPENTANE  | 1.0000              | ET-GLYCL         | 1.13E+04         | 62.07            | 5                          | 7                         |
| 43350 |                         | DIMETHYLETHER              | 1.0000              | ET-GLYCL         | 1.13E+04         | 62.07            | 5                          | 5                         |
| 43351 |                         | ETHYL ETHER                | 1.0000              | PR-GLYCL         | 1.76E+04         | 76.09            | 1                          | 1                         |
| 43367 |                         | GLYCOL ETHER               | 1.0000              | ET-GLYCL         | 1.13E+04         | 62.07            | 1                          | 1                         |
| 43368 |                         | GLYCOL                     | 1.0000              | RCHO-H           | 1.82E-11         | 118.18           | 3                          | 1                         |
| 43369 |                         | PROPYLENE GLYCOL           | 1.0000              | MEK-H            | 1.82E-11         | 118.18           |                            |                           |
| 43370 |                         | ETHYLENE GLYCOL            | 0.2000              |                  |                  |                  |                            |                           |
| 43371 |                         | HEXYLENE GLYCOL            | 0.6000              |                  |                  |                  |                            |                           |

(continued)

Table 17 (continued) - 7

| ID    | SET <sup>a</sup><br>NO. | Description                | Factor <sup>b</sup> | Model<br>Species | kOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech<br>Mix | Notes <sup>e</sup> |
|-------|-------------------------|----------------------------|---------------------|------------------|------------------|------------------|-----------------------------------|--------------------|
| 43404 |                         | ACETIC ACID                | 0.1000              | MEK-R            | 1.82E-11         | 118.18           |                                   |                    |
| 43432 |                         | METHYL ACETATE             | 0.1000              | A2A3-R           | 1.82E-11         | 118.18           | 2                                 | 1                  |
| 43433 |                         | ETHYL ACETATE              | 1.0000              | HCHO-R           | 6.00E-13         | 60.05            | 3                                 | 2                  |
| 43434 |                         | PROPYL ACETATE             | 1.0000              | RCHO-R           | 1.70E-13         | 74.08            | 3                                 | 1                  |
| 43435 |                         | N-BUTYL ACETATE            | 1.0000              | MEK-R            | 1.70E-12         | 88.10            | 3                                 | 2                  |
| 43438 |                         | ETHYL ACRYLATE             | 1.0000              | [N-C4]           | 4.20E-12         | 102.13           | 3                                 | 2                  |
| 43443 |                         | CELOSOLVE ACETATE          | 1.0000              | [N-C5]           | 4.30E-12         | 116.16           | 3                                 | 2                  |
| 43444 |                         | ISOPROPYL ACETATE          | 1.0000              | [1-BUTE]         | 4.56E+04         | 100.11           | 5                                 | 2                  |
| 43446 |                         | ISOBUTYL ACETATE           | 1.0000              | [N-C5]           | 1.96E-11         | 132.00           | 3                                 | 2                  |
| 43450 |                         | DIMETHYL FORMAMIDE         | 1.0000              | [ISO-C4]         | 3.09E-12         | 104.00           | 3                                 | 2                  |
| 43451 |                         | ISOBUTYL ISOBUTYRATE       | 1.0000              | [BR-C5]          | 5.40E-12         | 116.16           | 3                                 | 2                  |
| 43452 |                         | 2-ETHOXYETHYL ACETATE      | 1.0000              | RCHO             | 2.89E+04         | 73.09            | 5                                 | 2                  |
| 43502 |                         | FORMALDEHYDE               | 1.0000              | [BR-C7]          | 6.70E-12         | 144.21           | 3                                 | 2                  |
| 43503 |                         | ACETALDEHYDE               | 1.0000              | [N-C5]           | 1.85E-11         | 132.00           | 3                                 | 2                  |
| 43504 |                         | PROPRIONALDEHYDE           | 1.0000              | FORMALD          | 1.63E+04         | 30.03            | 1                                 | 1                  |
| 43505 |                         | ACROLEIN (ACRYLIC ALDHYDE) | 1.0000              | ACETALD          | 2.31E+04         | 44.05            | 1                                 | 1                  |
| 43510 |                         | BUTYRALDEHYDE              | 1.0000              | PROPALD          | 2.89E+04         | 58.08            | 1                                 | 1                  |
| 43511 |                         | C3 ALDEHYDE                | 1.0000              | ACROLEIN         | 2.89E+04         | 56.06            | 4                                 | 2                  |
| 43512 |                         | C5 ALDEHYDE                | 1.0000              | PROPALD          | 2.89E+04         | 72.12            | 3                                 | 2                  |
| 43513 | E                       | GLYOXAL                    | 1.0000              | PROPALD          | 2.89E+04         | 58.08            | 1                                 | 1                  |
| 43513 | A                       | C8 ALDEHYDE                | 1.0000              | ACETONE          | 2.89E+04         | 86.14            | 3                                 | 2                  |
| 43551 |                         | ACETONE                    | 1.0000              | MEK              | 2.89E+04         | 86.14            | 3                                 | 2                  |
| 43552 |                         | METHYL ETHYL KETONE        | 1.0000              | MEK              | 1.92E+03         | 72.10            | 1                                 | 1                  |
| 43559 |                         | METHYL N-BUTYL KETONE      | 1.0000              | MEK              | 1.92E+03         | 100.16           | 2                                 | 2                  |
| 43560 | E                       | METHYL ISOBUTYL KETONE     | 1.0000              | MEK              | 1.92E+03         | 100.16           | 2                                 | 2                  |
| 43561 | A                       | CYCLOHEXANONE              | 1.0000              | MEK              | 1.92E+03         | 98.15            | 4                                 | 2                  |
| 43561 | A                       | METHYL AMYL KETONE         | 1.0000              | MEK              | 1.92E+03         | 114.19           | 2                                 | 2                  |
| 43563 |                         | 2-METHYL-3-HEXANONE        | 1.0000              | MEK              | 1.92E+03         | 114.18           | 3                                 | 2                  |
| 43601 |                         | ETHYLENE OXIDE             | 1.0000              | HCHO-R           | 7.00E-14         | 44.05            | 3                                 | 2                  |
| 43602 |                         | PROPYLENE OXIDE            | 1.0000              | RCHO-R           | 5.20E-13         | 58.08            | 3                                 | 2                  |
| 43702 |                         | ACETONITRILE               | 1.0000              | INERT            | 2.12E-14         | 41.05            | 4                                 | 2                  |

(continued)

Table 17 (continued) - 8

| ID    | SET <sup>a</sup><br>NO. | Description                    | Factor <sup>b</sup> | Model<br>Species | kOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech Mix | Notes <sup>e</sup> |
|-------|-------------------------|--------------------------------|---------------------|------------------|------------------|------------------|--------------------------------|--------------------|
| 43704 |                         | ACRYLONITRILE                  | 1.0000              | HCHO-R           | 4.80E-12         | 53.06            | 5                              | 2                  |
| 43721 |                         | ETHYLAMINE                     | 1.0000              | ET-AMINE         | 2.76E-11         | 45.09            | 5                              | 2                  |
| 43740 |                         | TRIMETHYL AMINE                | 1.0000              | TM-AMINE         | 6.06E-11         | 59.11            | 5                              | 2                  |
| 43801 |                         | METHYL CHLORIDE                | 1.0000              | CL-ALK           | 4.48E-14         | 50.49            | 4                              | 2                  |
| 43802 |                         | DICHLOROMETHANE                | 1.0000              | CL-ALK           | 1.45E-13         | 84.94            | 4                              | 2                  |
| 43803 |                         | CHLOROFORM                     | 1.0000              | CL-ALK           | 1.06E-13         | 119.39           | 4                              | 2                  |
| 43804 |                         | CARBON TETRACHLORIDE           | 1.0000              | INERT            | 0.00E-01         | 153.84           | 1                              | 2                  |
| 43805 |                         | METHYLENE BROMIDE              | 1.0000              | CL-ALK           | 1.45E-13         | 173.85           | 5                              | 2                  |
| 43807 |                         | CARBON TETRABROMIDE            | 1.0000              | INERT            | 0.00E-01         | 331.67           | 1                              | 2                  |
| 43811 |                         | TRICHLOROFLUOROMETHANE         | 1.0000              | INERT            | 0.00E-01         | 137.38           | 1                              | 2                  |
| 43812 |                         | ETHYL CHLORIDE                 | 1.0000              | CL-ALK           | 4.00E-13         | 64.52            | 4                              | 2                  |
| 43813 |                         | 1,1-DICHLOROETHANE             | 1.0000              | CL-ALK           | 2.60E-13         | 98.97            | 4                              | 2                  |
| 43814 |                         | 1,1,1-TRICHLOROETHANE          | 1.0000              | CL-ALK           | 1.24E-14         | 133.42           | 4                              | 2                  |
| 43815 |                         | ETHYLENE DICHLORIDE            | 1.0000              | CL-OLE           | 2.30E-12         | 99.00            | 4                              | 2                  |
| 43817 |                         | PERCHLOROETHYLENE              | 1.0000              | CL-OLE           | 1.71E-13         | 165.85           | 4                              | 2                  |
| 43819 | A                       | METHYL BROMIDE                 | 1.0000              | CL-ALK           | 4.10E-14         | 94.95            | 4                              | 2                  |
| 43820 |                         | 1,1,2-TRICHLOROETHANE          | 1.0000              | CL-ALK           | 3.30E-13         | 131.66           | 4                              | 2                  |
| 43821 |                         | TRICHLOROTRIFLUOROETHANE       | 1.0000              | INERT            | 0.00E-01         | 187.38           | 1                              | 2                  |
| 43823 |                         | DICHLORODIFLUOROMETHANE (F-12) | 1.0000              | INERT            | 0.00E-01         | 120.91           | 1                              | 2                  |
| 43824 |                         | TRICHLOROETHYLENE              | 1.0000              | CL-OLE           | 2.34E-12         | 131.40           | 4                              | 2                  |
| 43826 |                         | CHLOROTRIFLUOROMETHANE (F-13)  | 1.0000              | INERT            | 0.00E-01         | 104.46           | 1                              | 2                  |
| 43827 |                         | CHLOROPENTAFLUOROETHANE(F-115) | 1.0000              | INERT            | 0.00E-01         | 154.47           | 1                              | 2                  |
| 43828 |                         | DICHLOROTETRAFLUOROETHANE/114  | 1.0000              | INERT            | 0.00E-01         | 170.92           | 1                              | 2                  |
| 43860 |                         | VINYL CHLORIDE                 | 1.0000              | CL-OLE           | 6.58E-12         | 62.50            | 4                              | 2                  |
| 43934 |                         | CARBON SULFIDE                 | 0.0066              | N-C8             | 1.20E+04         | 76.14            | 5                              | 0                  |
| 45101 |                         | NAPHTHA                        | 0.0803              | N-C9             | 1.40E+04         | 114.23           | 2                              | 5                  |
|       |                         |                                | 0.1141              | N-C10            | 1.61E+04         | 142.29           |                                |                    |
|       |                         |                                | 0.0873              | N-C11            | 1.82E+04         | 156.31           |                                |                    |
|       |                         |                                | 0.0268              | N-C12            | 2.02E+04         | 170.34           |                                |                    |
|       |                         |                                | 0.0030              | BR-C8            | 1.26E+04         | 114.23           |                                |                    |
|       |                         |                                | 0.0358              | BR-C9            | 1.54E+04         | 128.26           |                                |                    |
|       |                         |                                | 0.0509              | BR-C10           | 1.75E+04         | 142.29           |                                |                    |

(continued)

Table 17 (continued) - 9

| ID    | SET <sup>a</sup><br>NO. | Description               | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|---------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 45102 |                         | ISOMERS OF XYLENE         | 0.0388              | BR-C11           | 2.10E+04         | 156.31           |                            |                           |
| 45103 |                         | DIMETHYLETHYLBENZENE      | 0.0119              | BR-C12           | 2.30E+04         | 170.34           |                            |                           |
| 45104 |                         | ISOMERS OF ETHYLTOLUENE   | 0.1008              | CYC-C9           | 2.05E+04         | 126.24           |                            |                           |
| 45105 |                         | ISOMERS OF BUTYLBENZENE   | 0.2503              | CYC-C10          | 2.34E+04         | 140.27           |                            |                           |
| 45106 |                         | ISOMERS OF DIETHYLBENZENE | 0.1007              | CYC-C11          | 2.60E+04         | 154.30           |                            |                           |
| 45107 |                         | TRIMETHYLBENZENE          | 0.0185              | CYC-C12          | 2.89E+04         | 168.32           |                            |                           |
| 45108 |                         | PROPYLBENZENE             | 0.0630              | M-XYLENE         | 3.59E+04         | 106.17           |                            |                           |
| 45110 |                         | C10 AROMATIC              | 0.0031              | NAPHTHAL         | 3.11E+04         | 128.17           |                            |                           |
|       |                         |                           | 0.0010              | ME-NAPH          | 7.63E+04         | 142.20           |                            |                           |
|       |                         |                           | 0.0071              | TETRALIN         | 5.03E+04         | 132.21           |                            |                           |
|       |                         |                           | 1.0000              | ALK2BENZ         | 3.59E+04         | 106.16           | 2                          | 2                         |
|       |                         |                           | 1.0000              | ALK3BENZ         | 8.51E+04         | 134.21           | 2                          | 2                         |
|       |                         |                           | 1.0000              | ALK2BENZ         | 3.59E+04         | 120.19           | 2                          | 4                         |
|       |                         |                           | 1.0000              | ALK2BENZ         | 3.59E+04         | 134.21           | 2                          | 4                         |
|       |                         |                           | 1.0000              | ALK2BENZ         | 3.59E+04         | 134.21           | 2                          | 4                         |
|       |                         |                           | 1.0000              | ALK3BENZ         | 8.51E+04         | 120.19           | 2                          | 2                         |
|       |                         |                           | 1.0000              | ALK1BENZ         | 9.02E+03         | 120.19           | 2                          | 2                         |
|       |                         |                           | 0.2500              | ALK1BENZ         | 9.02E+03         | 134.22           | 2                          | 4                         |
|       |                         |                           | 0.5000              | ALK2BENZ         | 3.59E+04         | 134.22           |                            |                           |
|       |                         |                           | 0.2500              | ALK3BENZ         | 8.51E+04         | 134.22           |                            |                           |
| 45201 |                         | BENZENE                   | 1.0000              | BENZENE          | 1.89E+03         | 78.11            | 2                          | 1                         |
| 45202 |                         | TOLUENE                   | 1.0000              | TOLUENE          | 9.02E+03         | 92.13            | 2                          | 1                         |
| 45203 |                         | ETHYLBENZENE              | 1.0000              | C2-BENZ          | 1.10E+04         | 106.16           | 2                          | 2                         |
| 45204 |                         | O-XYLENE                  | 1.0000              | O-XYLENE         | 2.16E+04         | 106.16           | 2                          | 1                         |
| 45205 |                         | M-XYLENE                  | 1.0000              | M-XYLENE         | 3.59E+04         | 106.16           | 2                          | 1                         |
| 45206 |                         | P-XYLENE                  | 1.0000              | P-XYLENE         | 2.23E+04         | 106.16           | 2                          | 1                         |
| 45207 |                         | 1,3,5-TRIMETHYLBENZENE    | 1.0000              | 135-TMB          | 8.51E+04         | 120.19           | 2                          | 1                         |
| 45208 |                         | 1,2,4-TRIMETHYLBENZENE    | 1.0000              | 124-TMB          | 4.84E+04         | 120.19           | 2                          | 2                         |
| 45209 |                         | N-PROPYLBENZENE           | 1.0000              | I-C3-BEN         | 9.61E+03         | 120.19           | 2                          | 2                         |
| 45211 |                         | O-ETHYLTOLUENE            | 1.0000              | O-XYLENE         | 2.16E+04         | 120.19           | 2                          | 2                         |
| 45212 |                         | M-ETHYLTOLUENE            | 1.0000              | M-XYLENE         | 3.59E+04         | 120.19           | 2                          | 2                         |
| 45215 |                         | TERT-BUTYLBENZENE         | 1.0000              | ALK1BENZ         | 9.02E+03         | 134.21           | 2                          | 2                         |
| 45216 |                         | SEC-BUTYLBENZENE          | 1.0000              | S-C4-BEN         | 8.37E+03         | 134.21           | 2                          | 2                         |

(continued)

Table 17 (continued) - 10

| ID NO. | SET <sup>a</sup> NO. | Description            | Factor <sup>b</sup> | Model Species | kOH <sup>c</sup> | Molec. Weight | Codes <sup>d</sup> Mech | Mix | Notes <sup>e</sup> |
|--------|----------------------|------------------------|---------------------|---------------|------------------|---------------|-------------------------|-----|--------------------|
| 45217  |                      | 1,2 DIETHYLBENZENE     | 1.0000              | ALK2BENZ      | 3.59E+04         | 134.22        | 2                       | 2   |                    |
| 45218  |                      | M-DIETHYLBENZENE       | 1.0000              | ALK2BENZ      | 3.59E+04         | 134.22        | 2                       | 2   |                    |
| 45220  |                      | STYRENE                | 0.7402              | ALK1BENZ      | 9.02E+03         | 77.08         | 4                       | 2   |                    |
| 45221  |                      | A-METHYLSTYRENE        | 0.2598              | PROPENE       | 3.82E+04         | 27.06         |                         |     |                    |
|        |                      |                        | 0.6524              | ALK1BENZ      | 9.02E+03         | 77.08         | 4                       | 2   | 11                 |
|        |                      |                        | 0.3476              | ISOBUTEN      | 7.47E+04         | 41.07         |                         |     |                    |
| 45225  |                      | 1,2,3-TRIMETHYLBENZENE | 1.0000              | 123-TMB       | 4.84E+04         | 120.19        | 2                       | 2   |                    |
| 45232  | A                    | TETRAMETHYLBENZENE     | 1.0000              | ALK4BENZ      | 8.51E+04         | 134.21        | 2                       | 2   |                    |
| 45233  | A                    | TRI/TETRAALKYL BENZENE | 1.0000              | ALK3BENZ      | 8.51E+04         | 148.23        | 2                       | 2   |                    |
| 45234  |                      | METHYLPROPYLBENZENE    | 1.0000              | ALK2BENZ      | 3.59E+04         | 134.21        | 2                       | 2   |                    |
| 45238  |                      | ETHYLTOLUENE           | 1.0000              | ALK2BENZ      | 3.59E+04         | 120.20        | 2                       | 2   |                    |
| 45240  |                      | PROPYLBENZENE          | 1.0000              | ALK1BENZ      | 9.02E+03         | 120.20        | 2                       | 2   |                    |
| 45244  |                      | TETRAMETHYLBENZENE     | 1.0000              | ALK4BENZ      | 8.51E+04         | 134.21        | 2                       | 2   |                    |
| 45245  |                      | C5-ALKYLBENZENE        | 1.0000              | ALK1BENZ      | 9.02E+03         | 148.25        | 2                       | 2   |                    |
| 45300  |                      | PHENOLS                | 1.0000              | PHENOL        | 4.15E+04         | 94.11         | 2                       | 4   |                    |
| 45401  |                      | XYLENE BASE ACIDS      | 1.0000              | BENZALD       | 1.91E+04         | 150.13        | 5                       | 4   |                    |
| 45501  |                      | BENZALDEHYDE           | 1.0000              | BENZALD       | 1.91E+04         | 106.13        | 2                       | 1   |                    |
| 45801  |                      | MONOCHLOROBENZENE      | 1.0000              | BENZENE       | 9.40E-13         | 112.56        | 4                       | 2   |                    |
| 45807  |                      | P-DICHLOROBENZENE      | 1.0000              | BENZENE       | 3.20E-13         | 147.01        | 4                       | 2   |                    |
| 46701  |                      | NAPHTHALENE            | 1.0000              | NAPHTHAL      | 3.11E+04         | 128.19        | 2                       | 1   |                    |
| 46702  |                      | METHYL NAPHTHALENES    | 1.0000              | ME-NAPH       | 7.63E+04         | 142.20        | 2                       | 2   |                    |
| 90005  |                      | 2,5 DIMETHYLHEPTANE    | 1.0000              | BR-C9         | 1.54E+04         | 128.26        | 2                       | 2   |                    |
| 90009  |                      | 2,4,5-TRIMETHYLHEPTANE | 1.0000              | BR-C10        | 1.75E+04         | 142.28        | 2                       | 2   |                    |
| 90010  |                      | M-XYLENE AND P-XYLENE  | 0.5000              | M-XYLENE      | 3.59E+04         | 134.22        | 2                       | 2   |                    |
|        |                      |                        | 0.5000              | M-XYLENE      | 3.59E+04         | 134.22        |                         |     |                    |
| 90021  |                      | METHYLPROPANE          | 1.0000              | ISO-C4        | 3.50E+03         | 58.12         | 1                       | 1   |                    |
| 90026  |                      | METHYL PENTANE         | 1.0000              | BR-C6         | 7.93E+03         | 86.17         | 1                       | 2   |                    |
| 90028  |                      | METHYLHEXANE           | 1.0000              | BR-C7         | 1.05E+04         | 100.20        | 2                       | 2   |                    |
| 90042  |                      | T-3-HEXENE             | 1.0000              | C6-OLE2       | 9.24E+04         | 84.16         | 2                       | 2   |                    |
| 90060  |                      | DIMETHYL BUTANE        | 1.0000              | 23-DMB        | 7.99E+03         | 86.18         | 1                       | 4   |                    |
| 90067  |                      | DIMETHYLHEXANE         | 1.0000              | BR-C8         | 1.26E+04         | 114.23        | 2                       | 2   |                    |
| 90081  |                      | ETHYLHEXANE            | 1.0000              | BR-C8         | 1.26E+04         | 114.23        | 2                       | 2   |                    |
| 90104  |                      | METHYLOCTANE           | 1.0000              | BR-C9         | 1.54E+04         | 128.26        | 2                       | 2   |                    |

(continued)

Table 17 (continued) - 11

| ID NO. | SET <sup>a</sup> | Description             | Factor <sup>b</sup> | Model Species | KOH <sup>c</sup> | Molec. Weight | Codes <sup>d</sup> Mech | Notes <sup>e</sup> Mix |
|--------|------------------|-------------------------|---------------------|---------------|------------------|---------------|-------------------------|------------------------|
| 98001  |                  | 2,3-DIMETHYLBUTANE      | 1.0000              | 23-DMB        | 7.99E+03         | 86.17         | 1                       | 1                      |
| 98002  |                  | 2-ETHYL-1-BUTENE        | 1.0000              | C6-OLE1       | 5.37E+04         | 84.16         | 2                       | 2                      |
| 98003  |                  | C-3-HEXENE              | 1.0000              | C6-OLE2       | 9.24E+04         | 84.16         | 2                       | 2                      |
| 98004  |                  | 2-METHYL-2-PENTENE      | 1.0000              | C6-OLE2       | 9.24E+04         | 84.16         | 2                       | 2                      |
| 98005  |                  | 1-HEPTENE               | 1.0000              | C7-OLE1       | 5.37E+04         | 98.18         | 2                       | 2                      |
| 98010  |                  | METHYLNAPHTHALENE       | 1.0000              | ALK1NAPH      | 7.63E+04         | 142.19        | 2                       | 2                      |
| 98011  |                  | ETHYLNAPHTHALENE        | 1.0000              | ALK1NAPH      | 7.63E+04         | 156.22        | 2                       | 2                      |
| 98012  |                  | DIMETHYLNAPHTHALENE     | 1.0000              | ALK2NAPH      | 1.13E+05         | 156.22        | 2                       | 2                      |
| 98013  |                  | PROPYLNAPHTHALENE       | 1.0000              | ALK1NAPH      | 7.63E+04         | 170.25        | 2                       | 2                      |
| 98014  |                  | TRIMETHYLNAPHTHALENE    | 1.0000              | ALK3NAPH      | 1.13E+05         | 170.25        | 2                       | 2                      |
| 98015  |                  | ANTHRACENE              | 1.0000              | NAPHTHAL      | 3.11E+04         | 178.22        | 4                       | 2                      |
| 98016  |                  | METHYLANTHRACENE        | 1.0000              | ALK1NAPH      | 7.63E+04         | 192.25        | 4                       | 2                      |
| 98018  |                  | DIMETHYL ETHER          | 1.0000              | ME-O-ME       | 4.42E+03         | 46.07         | 2                       | 1                      |
| 98021  |                  | O-CRESOL (2-M-BENZENOL) | 1.0000              | CRESOL        | 5.87E+04         | 110.16        | 2                       | 1                      |
| 98022  |                  | M-CRESOL (3-M-BENZENOL) | 1.0000              | CRESOL        | 5.87E+04         | 110.16        | 2                       | 2                      |
| 98023  |                  | P-CRESOL (4-M-BENZENOL) | 1.0000              | CRESOL        | 5.87E+04         | 110.16        | 2                       | 2                      |
| 98025  |                  | A-PINENE                | 1.0000              | A-PINENE      | 7.73E+04         | 136.24        | 3                       | 2                      |
| 98026  |                  | B-PINENE                | 1.0000              | B-PINENE      | 1.14E+05         | 136.24        | 3                       | 2                      |
| 98027  |                  | D-LIMONENE              | 1.0000              | A-PINENE      | 1.70E-10         | 136.24        | 3                       | 2                      |
| 98030  |                  | CARBON SULFIDE          | 1.0000              | INERT         | 0.00E-01         | 76.14         | 5                       | 0                      |
| 98031  |                  | CARBONYL SULFIDE        | 1.0000              | INERT         | 0.00E-01         | 60.08         | 5                       | 0                      |
| 98032  |                  | 3,5,5-TRIMETHYLHEXANE   | 1.0000              | BR-C9         | 1.54E+04         | 128.26        | 2                       | 2                      |
| 98033  |                  | 2,2,5-TRIMETHYLHEXANE   | 1.0000              | BR-C9         | 1.54E+04         | 128.26        | 2                       | 2                      |
| 98034  |                  | T-2-HEXENE              | 1.0000              | C6-OLE2       | 9.24E+04         | 84.16         | 2                       | 2                      |
| 98035  |                  | C-2-HEXENE              | 1.0000              | C6-OLE2       | 9.24E+04         | 84.16         | 2                       | 2                      |
| 98036  |                  | ISOBUTYRALDEHYDE        | 1.0000              | PROPALD       | 2.89E+04         | 72.11         | 3                       | 2                      |
| 98037  | E                | 1-METHYLCLOHEXENE       | 1.0000              | C7-OLE2       | 9.24E+04         | 96.17         | 3                       | 2                      |
| 98037  | A                | 1-METHYLCLOHEXANE       | 1.0000              | CYC-C7        | 1.50E+04         | 98.19         | 2                       | 2                      |
| 98038  |                  | C9 OLEFINS              | 0.5000              | C9-OLE1       | 5.37E+04         | 127.05        | 2                       | 4                      |
| 98039  |                  | C10 OLEFINS             | 0.5000              | C10-OLE1      | 5.37E+04         | 140.27        | 2                       | 4                      |
| 98040  |                  | 2-METHYL-1-PENTENE      | 0.5000              | C10-OLE2      | 9.24E+04         | 140.27        | 2                       | 2                      |
|        |                  |                         | 1.0000              | C6-OLE1       | 5.37E+04         | 84.16         | 2                       |                        |

(continued)

Table 17 (continued) - 12

| ID    | SET <sup>a</sup><br>NO. | Description                | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|----------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 98041 |                         | 3-HEPTENE                  | 1.0000              | C7-OLE2          | 9.24E+04         | 98.19            | 2                          | 2                         |
| 98042 |                         | 4-NONENE                   | 1.0000              | C9-OLE2          | 9.24E+04         | 126.24           | 2                          | 2                         |
| 98043 |                         | ISOPROPYLBENZENE (CUMENE)  | 1.0000              | I-C3-BEN         | 9.61E+03         | 120.20           | 2                          | 2                         |
| 98044 |                         | INDAN                      | 1.0000              | TETRALIN         | 5.03E+04         | 118.18           | 4                          | 2                         |
| 98045 |                         | M-DIETHYLBENZENE           | 1.0000              | M-XYLENE         | 3.59E+04         | 134.22           | 2                          | 2                         |
| 98046 |                         | NAPHTHALENE                | 1.0000              | NAPHTHAL         | 3.11E+04         | 128.19           | 2                          | 1                         |
| 98047 |                         | ISOBUTYLBENZENE            | 1.0000              | S-C4-BEN         | 8.37E+03         | 134.22           | 2                          | 2                         |
| 98048 |                         | INDENE                     | 1.0000              | ALK2BENZ         | 3.59E+04         | 116.16           | 4                          | 2                         |
| 98049 |                         | C9 AROMATICS               | 0.2500              | ALK1BENZ         | 9.02E+03         | 120.20           | 2                          | 4                         |
|       |                         |                            | 0.5000              | ALK2BENZ         | 3.59E+04         | 120.20           |                            |                           |
|       |                         |                            | 0.2500              | ALK3BENZ         | 8.51E+04         | 120.20           |                            |                           |
|       |                         |                            | 0.2500              | ALK1BENZ         | 9.02E+03         | 134.22           | 2                          |                           |
|       |                         |                            | 0.5000              | ALK2BENZ         | 3.59E+04         | 134.22           |                            |                           |
| 98050 |                         | C10 AROMATICS              | 0.2500              | ALK3BENZ         | 8.51E+04         | 134.22           | 2                          |                           |
|       |                         |                            | 0.2500              | ALK1BENZ         | 9.02E+03         | 134.22           |                            |                           |
|       |                         |                            | 0.5000              | ALK2BENZ         | 3.59E+04         | 134.22           |                            |                           |
| 98052 |                         | T-BUTYLBENZENE             | 1.0000              | ALK3BENZ         | 8.51E+04         | 134.22           | 2                          | 2                         |
| 98054 |                         | 2,4,4-TRIMETHYL-1-PENTENE  | 1.0000              | C8-OLE1          | 5.37E+04         | 112.22           | 2                          | 2                         |
| 98055 |                         | 2,4,4-TRIMETHYL-2-PENTENE  | 1.0000              | C8-OLE2          | 9.24E+04         | 112.22           | 2                          | 2                         |
| 98056 |                         | ISOVALERALDEHYDE           | 1.0000              | PROALD           | 2.89E+04         | 86.14            | 3                          | 2                         |
| 98057 |                         | ETHYL CYCLOPENTANE         | 1.0000              | CYC-C7           | 1.50E+04         | 98.19            | 2                          | 2                         |
| 98058 |                         | TRIMETHYL CYCLOPENTANE     | 1.0000              | CYC-C8           | 1.79E+04         | 112.22           | 2                          | 2                         |
| 98059 |                         | DIMETHYL CYCLOHEXANE       | 1.0000              | CYC-C8           | 1.79E+04         | 112.22           | 2                          | 2                         |
| 98060 |                         | TRIMETHYL CYCLOHEXANE      | 1.0000              | CYC-C9           | 2.05E+04         | 126.24           | 2                          | 2                         |
| 98061 |                         | ETHYL CYCLOHEXANE          | 1.0000              | CYC-C8           | 1.79E+04         | 112.22           | 2                          | 2                         |
| 98062 |                         | DIETHYL CYCLOHEXANE        | 1.0000              | CYC-C10          | 2.34E+04         | 140.27           | 2                          | 2                         |
| 98063 |                         | N-PENTYL CYCLOHEXANE       | 1.0000              | CYC-C11          | 2.60E+04         | 154.30           | 2                          | 2                         |
| 98064 |                         | C2 CYCLOHEXANE             | 1.0000              | CYC-C8           | 1.79E+04         | 112.22           | 2                          | 2                         |
| 98065 |                         | C3 CYCLOHEXANE             | 1.0000              | CYC-C9           | 2.05E+04         | 126.24           | 2                          | 2                         |
| 98066 |                         | C4 CYCLOHEXANE             | 1.0000              | CYC-C10          | 2.34E+04         | 140.27           | 2                          | 2                         |
| 98067 |                         | C5 CYCLOHEXANE             | 1.0000              | CYC-C11          | 2.60E+04         | 154.30           | 2                          | 2                         |
| 98068 |                         | C3 ALKYL CYCLOHEXANE       | 1.0000              | CYC-C9           | 2.05E+04         | 126.24           | 2                          | 2                         |
| 98069 |                         | C4 ALKYL CYCLOHEXANE       | 1.0000              | CYC-C10          | 2.34E+04         | 140.27           | 2                          | 2                         |
| 98070 |                         | C4 SUBSTITUTED CYCLOHEXANE | 1.0000              | CYC-C10          | 2.34E+04         | 140.27           | 2                          | 2                         |
| 98071 |                         | C5 SUBSTITUTED CYCLOHEXANE | 1.0000              | CYC-C11          | 2.60E+04         | 154.30           | 2                          | 2                         |

(continued)

Table 17 (continued) - 13

| ID NO. | SET <sup>a</sup> NO. | Description                  | Factor <sup>b</sup> | Model Species | KOH <sup>c</sup> | Molec. Weight | Codes <sup>d</sup> Mech | Mix | Notes <sup>e</sup> |
|--------|----------------------|------------------------------|---------------------|---------------|------------------|---------------|-------------------------|-----|--------------------|
| 98072  | C6                   | SUBSTITUTED CYCLOHEXANE      | 1.0000              | CYC-C12       | 2.89E+04         | 168.32        | 2                       | 2   |                    |
| 98073  | C4                   | SUBSTITUTED CYCLOHEXANONE    | 1.0000              | MEK           | 1.92E+03         | 154.26        | 3                       | 2   |                    |
| 98074  |                      | BUTYL CELLOSOLVE             | 0.3500              | A1A3-R        | 1.96E-11         | 118.17        | 3                       | 2   | 13                 |
|        |                      |                              | 0.2000              | RCHO-H        | 1.96E-11         | 118.17        |                         |     |                    |
|        |                      |                              | 0.4500              | [N-C6]        | 1.96E-11         | 118.17        |                         |     |                    |
| 98075  | C5                   | ESTER                        | 1.0000              | [N-C4]        | 4.20E-12         | 102.13        | 3                       | 4   | 14                 |
| 98076  |                      | 2-METHYL-3-HEXANONE          | 1.0000              | MEK           | 1.92E+03         | 114.19        | 3                       | 2   |                    |
| 98077  |                      | HEPTANONE                    | 1.0000              | MEK           | 1.92E+03         | 114.18        | 3                       | 2   |                    |
| 98079  |                      | TERPINENE                    | 1.0000              | A-PINENE      | 3.60E-10         | 136.23        | 3                       | 2   |                    |
| 98080  | A                    | BUTANDIOL                    | 0.2500              | RCHO-H        | 1.54E-11         | 90.12         | 3                       | 4   | 15                 |
|        |                      |                              | 0.7500              | MEK-H         | 1.54E-11         | 90.12         |                         |     |                    |
| 98082  |                      | ETHYLHEPTENE                 | 1.0000              | C9-OLE1       | 5.37E+04         | 127.05        | 2                       | 4   | 16                 |
| 98083  |                      | TRIMETHYLDECENE              | 1.0000              | C13-OLE2      | 9.24E+04         | 182.35        | 2                       | 4   | 17                 |
| 98084  | C2                   | ALKYL INDAN                  | 1.0000              | TETRALIN      | 5.03E+04         | 146.23        | 4                       | 2   |                    |
| 98085  |                      | ALKYL SUSTITUTED CYCLOHEXANE | 1.0000              | CYC-C9        | 2.05E+04         | 126.24        | 2                       | 2   |                    |
| 98086  | C2                   | ALKYL DECALIN                | 1.0000              | CYC-C12       | 2.89E+04         | 166.27        | 2                       | 2   |                    |
| 98086  |                      | METHYL HEPTENE               | 1.0000              | C9-OLE1       | 5.37E+04         | 112.22        | 2                       | 4   | 16                 |
| 98090  |                      | DIMETHYLHEPTANE              | 1.0000              | BR-C9         | 1.54E+04         | 128.26        | 2                       | 2   |                    |
| 98091  |                      | PENTYL ALCOHOL               | 0.5000              | RCHO-H        | 7.77E-12         | 88.15         | 3                       | 4   |                    |
| 98094  |                      |                              | 0.5000              | [N-C5]        | 7.77E-12         | 88.15         |                         |     |                    |
| 98095  | C6                   | ALDEHYDE                     | 1.0000              | PROPALD       | 2.89E+04         | 100.17        | 3                       | 2   |                    |
| 98096  |                      | CARBITOL                     | 0.1300              | RCHO-H        | 2.88E-11         | 134.17        | 3                       | 2   |                    |
|        |                      |                              | 0.8700              | [N-C6]        | 2.88E-11         | 134.17        |                         |     |                    |
| 98098  |                      | PARAFFIN BOND                | 0.0952              | N-C4          | 3.75E+03         | 58.12         | 4                       | 0   | 18                 |
|        |                      |                              | 0.1231              | N-C5          | 5.81E+03         | 75.12         |                         |     |                    |
|        |                      |                              | 0.0952              | ISO-C4        | 3.50E+03         | 58.12         |                         |     |                    |
|        |                      |                              | 0.1231              | ISO-C5        | 5.87E+03         | 75.12         |                         |     |                    |
|        |                      |                              | 0.0706              | N-C6          | 7.87E+03         | 86.18         |                         |     |                    |
|        |                      |                              | 0.0821              | N-C7          | 9.92E+03         | 100.21        |                         |     |                    |
|        |                      |                              | 0.0936              | N-C8          | 1.20E+04         | 114.23        |                         |     |                    |
|        |                      |                              | 0.0706              | 23-DMB        | 7.99E+03         | 86.18         |                         |     |                    |
|        |                      |                              | 0.0706              | 2-ME-C5       | 7.93E+03         | 86.18         |                         |     |                    |
|        |                      |                              | 0.0821              | 23-DM-C5      | 1.06E+04         | 100.21        |                         |     |                    |

(continued)

Table 17 (continued) - 14

| ID    | SET <sup>a</sup><br>NO. | Description                | Factor <sup>b</sup>   | Model<br>Species   | KOH <sup>c</sup>   | Molec.<br>Weight  | Codes <sup>d</sup><br>Mech | Mix | Notes <sup>e</sup> |
|-------|-------------------------|----------------------------|---|--|--|---|----------------------------|-----|--------------------|
| 98099 |                         | OLEFIN BOND                | 0.0936<br>1.0198<br>0.6799<br>-0.0669<br>-0.0831<br>-0.0669<br>-0.0831<br>-0.0501<br>-0.0583<br>-0.0664<br>-0.0501<br>-0.0501<br>-0.0583<br>-0.0664 | ISO-C8<br>PROPENE<br>T-2-BUTE<br>N-C4<br>N-C5<br>ISO-C4<br>ISO-C5<br>N-C6<br>N-C7<br>N-C8<br>23-DMB<br>2-ME-C5<br>23-DM-C5<br>ISO-C8 | 6.88E+03<br>3.82E+04<br>9.24E+04<br>3.75E+03<br>5.81E+03<br>3.50E+03<br>5.87E+03<br>7.87E+03<br>9.92E+03<br>1.20E+04<br>7.99E+03<br>7.93E+03<br>1.06E+04<br>6.88E+03 | 114.23<br>42.08<br>56.11<br>58.12<br>72.15<br>58.12<br>72.15<br>86.18<br>100.21<br>114.23<br>86.18<br>86.18<br>100.21<br>114.23 | 5<br>4                     | 19  |                    |
| 98100 |                         | ETHYLENE BOND              | 1.0000  | ETHENE   | 1.24E+04   | 28.05   | 1                          | 1   |                    |
| 98103 |                         | UNREACTIVE BOND            | 1.0000  | INERT  | 0.00E-01   | 16.00   | 1                          | 2   |                    |
| 98104 |                         | 1-CHLOROBUTANE             | 1.0000  | N-C4   | 3.07E-12   | 92.57   | 4                          | 2   | 6                  |
| 98105 |                         | 3-(CHLOROMETHYL)-HEPTANE   | 1.0000  | BR-C8  | 1.26E+04   | 148.68  | 4                          | 2   | 6                  |
| 98106 |                         | ETHYL ISOPROPYL ETHER      | 1.0000  | [BR-C5]  | 1.69E-11   | 88.15   | 3                          | 2   | 6                  |
| 98107 |                         | DIBUTYL ETHER              | 1.0000  | [N-C8]   | 1.89E-11   | 130.23  | 3                          | 2   | 6                  |
| 98108 |                         | 2-BUTYL TETRAHYDROFURAN    | 1.0000  | [CYC-C8]   | 2.64E-11   | 128.19  | 3                          | 2   | 6                  |
| 98109 |                         | PROPYLCYCLOHEXANONE        | 1.0000  | MEK  | 1.92E+03   | 140.23  | 3                          | 2   | 6                  |
| 98110 |                         | 2-(2-BUTOXYETHOXY)-ETHANOL | 0.1000  | RCHO-H   | 3.28E-11   | 162.18  | 3                          | 2   | 6                  |
| 98111 |                         | 1-ETHOXY-2-PROPANOL        | 0.9000  | [N-C8]   | 3.28E-11   | 162.18  | 3                          | 1   | 20                 |
| 98112 |                         | 2-ETHYL-1-HEXANOL          | 0.4000  | MEK-H  | 2.01E-11   | 104.15  | 3                          | 1   |                    |
| 98113 |                         | 1-HEPTANOL                 | 0.3000  | MEK-R  | 2.01E-11   | 104.15  |                            |     |                    |
| 98114 |                         | METHYL ISOBUTYRATE         | 0.3000  | A2A3-R   | 2.01E-11   | 104.15  |                            |     |                    |
| 98115 |                         | ISOAMYL ISOBUTYRATE        | 0.7000  | [BR-C8]  | 1.30E-11   | 130.23  | 3                          | 2   | 6                  |
|       |                         |                            | 0.3500  | RCHO-H   | 1.06E-11   | 116.21  | 3                          | 2   | 6                  |
|       |                         |                            | 0.6500  | [N-C7]   | 1.06E-11   | 116.21  |                            |     |                    |
|       |                         |                            |   | RCHO-R   | 5.90E-13   | 102.13  | 3                          | 2   | 6                  |
|       |                         |                            |   | [BR-C8]  | 6.75E-12   | 158.24  | 3                          | 2   | 6                  |

(continued)

Table 17 (continued) - 15

| ID    | SET <sup>a</sup><br>NO. | Description                 | Factor <sup>b</sup> | Model<br>Species | KOH <sup>c</sup> | Molec.<br>Weight | Codes <sup>d</sup><br>Mech | Notes <sup>e</sup><br>Mix |
|-------|-------------------------|-----------------------------|---------------------|------------------|------------------|------------------|----------------------------|---------------------------|
| 98116 |                         | SUBSTITUTED C7 ESTER (C12)  | 1.0000              | [BR-C8]          | 6.75E-12         | 158.24           | 5                          | 5 21                      |
| 98117 |                         | SUBSTITUTED C9 ESTER (C12)  | 1.0000              | [BR-C8]          | 6.75E-12         | 158.24           | 5                          | 5 21                      |
| 98118 |                         | METHYL ACRYLATE             | 1.0000              | [1-BUTE]         | 4.56E+04         | 86.09            | 5                          | 2                         |
| 98119 |                         | VINYL ACETATE               | 1.0000              | [1-BUTE]         | 4.56E+04         | 86.09            | 5                          | 2                         |
| 99009 |                         | NITROBENZENE                | 1.0000              | BENZENE          | 2.10E-13         | 123.11           | 4                          | 2                         |
| 99013 |                         | 1,1-DICHLOROETHENE          | 1.0000              | CL-OLE           | 8.10E-12         | 96.95            | 4                          | 2                         |
| 99014 |                         | ETHYLENE DIBROMIDE          | 1.0000              | CL-OLE           | 2.30E-12         | 187.88           | 4                          | 2 22                      |
| 99016 |                         | 1,2-DICHLOROPROPANE         | 1.0000              | CL-ALK           | 9.90E-13         | 112.99           | 4                          | 2 6                       |
| 99018 |                         | TRANS- 1,2-DICHLOROETHENE   | 1.0000              | CL-OLE           | 1.80E-12         | 96.95            | 4                          | 2                         |
| 99021 |                         | 3-CARENE                    | 1.0000              | A-PINENE         | 8.70E-11         | 136.23           | 3                          | 2                         |
| 99024 |                         | M & P-XYLENE                | 1.0000              | ALK2BENZ         | 3.59E+04         | 106.16           | 2                          | 2                         |
| 99901 |                         | 1-OCTENE                    | 1.0000              | C8-OLE1          | 5.37E+04         | 112.21           | 2                          | 2                         |
| 99902 |                         | FURAN                       | 1.0000              | FURAN            | 3.59E+04         | 68.08            | 2                          | 1                         |
| 99903 |                         | GLYOXAL                     | 1.0000              | GLYOXAL          | 1.64E+04         | 58.04            | 1                          | 1                         |
| 99905 |                         | ISOMERS OF HEXENE           | 0.5000              | C6-OLE1          | 5.37E+04         | 84.16            | 2                          | 4                         |
| 99906 |                         | ISOMERS OF OCTENE           | 0.5000              | C6-OLE2          | 9.24E+04         | 84.16            |                            |                           |
| 99911 |                         | 3,4 DIMETHYLOCTANE          | 0.5000              | C8-OLE1          | 5.37E+04         | 112.21           | 2                          | 4                         |
| 99912 |                         | 1-METHYL-3-ETHYLBENZENE     | 1.0000              | C8-OLE2          | 9.24E+04         | 112.21           |                            |                           |
| 99913 |                         | 1-METHYL-2-ETHYLBENZENE     | 1.0000              | BR-C10           | 1.75E+04         | 142.28           | 2                          | 2                         |
| 99915 |                         | ISOBUTYLBENZENE             | 1.0000              | ALK2BENZ         | 3.59E+04         | 120.20           | 2                          | 2                         |
| 99917 |                         | 1-METHYL-3-ISOPROPYLBENZENE | 1.0000              | ALK1BENZ         | 9.02E+03         | 134.22           | 2                          | 2                         |
| 99918 |                         | 2-METHYLDECAANE             | 1.0000              | ALK2BENZ         | 3.59E+04         | 134.22           | 2                          | 2                         |
|       |                         |                             |                     | BR-C11           | 2.10E+04         | 156.31           | 2                          | 2                         |

<sup>a</sup>A nonblank symbol is given in this column when different species are used for this SAROAD number in the ARB and the EPA/NAPAP data sets. "A" = ARB assignment, "E" = EPA/NAPAP assignment.

<sup>b</sup>This factor gives the relative amount of each model species used for SAROAD classes which are represented by mixtures of model species.

(continued)

<sup>c</sup>Rate constants are in units of ppm<sup>-1</sup> min<sup>-1</sup>. The rate constant is for the model species used to represent the SAROAD class, and not necessarily the specific compound being represented.

<sup>d</sup>These codes refer to the uncertainty in the mechanism, and the way the emitted species is represented, and the degree of characterization for SAROAD classes which are mixtures. The codes for the mechanistic uncertainty ("Mech") are as follows:

- 0 = Code not assigned.
- 1 = Mechanism considered to be reasonably well established.
- 2 = Mechanism not as well established.
- 3 = Mechanism or appropriateness of representation used is uncertain.
- 4 = Mechanism or appropriateness of representation used is highly uncertain.
- 5 = Mechanism is extremely uncertain, and the representation used for it is probably inappropriate.

The codes used for the representation method or mixture characterization ("Mix") are as follows:

- 0 = Code not assigned
- 1 = This compound is explicitly represented by the detailed model species used.
- 2 = This compound or mixture is lumped with other compounds considered to have comparable reactivity.
- 3 = This is a mixture. A "typical" composition is given.
- 4 = The composition of this mixture is uncertain or poorly characterized, at least with respect to reactivity. Should not be used in emissions profiles.
- 5 = This is an extremely poorly characterized mixture. Should never be used in emissions profiles.

<sup>e</sup>The notes for the specific SAROAD classes are as follows:

- 1) The composition used for this mixture is based on the composition assigned for "Mineral Spirits 75 - Beaumont," derived from Union Oil Co. data sheet supplied by Dunn-Edwards Co. for a solvent reactivity consulting project. (July 15, 1987).
- 2) This is combined with "99904 ISOMERS OF HEPTENE" used in the assignments given by Lurmann et al. (1987a)
- 3) This is CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH. Also called BUTYL CELLOSOLVE.
- 4) This is also called METHYL CELLOSOLVE.
- 5) This is also called CELLOSOLVE. The rate constant and mechanism are estimated. Mechanism estimate based on: 25% RCHO + HCHO + HO<sub>2</sub>-R; and 35% RCHO + RO<sub>2</sub>-R.
- 6) Rate constant estimated.

(continued)

Table 17 (continued) - 17

- 7) Unknown what this is. Parameters for ethylene glycol were used, since it has the same molecular weight on the ARB file.
- 8) Assumed to be 1,2-dihydroxy hexane. Rate constant and mechanism estimated. Mechanism estimated to be: 60% MEK + HO<sub>2</sub>; 20% RCHO + HO<sub>2</sub>; 10% MEK + RO<sub>2</sub>-R; and 10% CCHO + RO<sub>2</sub>-R.
- 9) Represented by dichloromethane
- 10) Average of estimated rate constants for 1,1-, cis- and trans-1,2-DCE used.
- 11) This is assumed to be Bz-C(C)=C.
- 12) This is supposedly terephthalic acid, or p-carboxy benzaldehyde. Represented by benzaldehyde.
- 13) Rate constant and mechanism estimated. Estimated 20% reaction at position alpha to -OH, 35% beta.
- 14) Probably is propyl acetate. So same assignment as 43434.
- 15) Estimated rate constant. Assigned based on 1,2-butandiol.
- 16) Name is ambiguous. Assumed to be a 1-alkene.
- 17) Name is ambiguous. Assumed to be a 2-alkene.
- 18) Distribution of species used to represent this class were derived based on assuming that the amounts of carbon bond species were derived using mixtures with the same alkane composition as in the default NMOC species composition recommended by Lurmann et al. (1987a) for the surface layer, given in terms of the model species used in the condensed SAPRC/ERT mechanism. This distribution should be updated based on mixture being simulated, or -- better yet -- this class should not be used in emissions profiles.
- 19) Distribution of species used to represent this class were derived based on assuming that the amounts of carbon bond species were derived using mixtures with the same non-ethene olefin composition as in the default NMOC species composition recommended by Lurmann et al. (1987a) for the surface layer, given in terms of the model species used in the condensed SAPRC/ERT mechanism. It is assumed that ethene is not lumped into this group. This distribution depends on the mixture being simulated.
- 20) The rate constant and mechanism were estimated. Mechanism estimated to consist of 40% MEK + HO<sub>2</sub>; 30% MEK + RO<sub>2</sub>-R; and 30% CCHO + RCHO + RO<sub>2</sub>-R.
- 21) This is poorly characterized. A C12 ester is not likely to have much of a vapor pressure, but it may decompose to form more volatile species. Arbitrarily represented by isoamyl isobutyrate. (See 98115)
- 22) Same representation as ethylene dichloride.

ambiguous as to the relative importance of alkenes with terminal double bonds compared to those where the double bonds are in an internal position, double bonds, which are significantly more reactive. In those cases, we arbitrarily assumed that these classes consisted of equal amounts of both types of alkenes, but this may well not be appropriate. [Indeed, we should note that when confronted with the same problem, Jeffries et al. (1987) assumed that all these alkenes are terminal.] An analogous problem occurs in SAROAD classes for isomers of aromatic hydrocarbons, where the number of substituents about the aromatic ring is ambiguous. Since the reactivity of aromatics tend to increase significantly with number of substituents about the ring, we also had to make arbitrary assignments in those cases. (On the other hand, the many classes referring to isomers of alkanes do not present such a problem, since we presently represent all branched alkanes with a given number of carbons as having the same reaction mechanism.) The presence of these poorly characterized chemical categories in the present emissions data sets introduces additional uncertainties in the representation of emissions in airshed models, beyond the already significant uncertainties in the atmospheric reactions of many of the emitted compounds themselves.